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PNNL- 31953

In situ study of Crystal Surface Interactions Guided by Biomolecules or Ligands

September 2021

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Zexi Lu

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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Acknowledgments

The author would like to thank the following for their contributions to this work.

Theoretical Simulations and Calculations

Pacific Northwest National Laboratory: Zexi Lu, Peter Sushko

AFM measurement

Pacific Northwest National Laboratory: Jaewon Lee, Jaeyoung Heo

AFM discussion

Pacific Northwest National Laboratory: Elias Nakouzi, Ben Legg

Contents

1.0 Background and Significance

Emergent physical and chemical properties are inherently tied to structures, sizes, and geometries of materials [1]. Particle assembly is recognized as a common pathway for crystal growth in both natural and synthetic systems, leading to a wide variety of complex structures. In synthetic systems, hierarchical nanostructures (e.g., highly branched nanowires [2]) and superlattices (e.g., three-dimensional photonic crystals [3]) crystalize through non-classical pathways of nucleation and growth, such as assembly of nanoparticles. Ligands or biomolecules commonly exist and play a key role in particle-mediated material growth. Ligands or surfactants are used in synthesis processes to control material structures, such as mesoporous materials, by tuning hydrophilic and hydrophobic groups in ligands/surfactants and their concentration [4]. In nature, guided by biomolecules, crystals grow into various complex structures with unique properties [5]. Sequence-defined peptoids with functional groups existing as side chains have been successfully used to control the synthesis of highly branched plasmonic gold particles [6]. Specialized proteins and peptides can precisely control crystal nucleation, growth kinetics, phase, and morphology.

However, no quantitative framework exists to describe these processes. It is not fully understood how these organic molecules affect the forces that interact between particles and thus the dynamics of particle assembly and the resulting structures. Specifically, through what functional groups do the crystal surface and organic molecules bind? How does it affect interactions between particles? What are the roles of the functional groups, such as hydrophobic and hydrophilic groups, in the particle assembly? How does the specific arrangement of hydrophilic and hydrophobic groups in side chains determine the interfacial structures of the solid/liquid, i.e. solvent/ligand (biomolecule)/crystal surface, affect the forces interacting between particles, and thus control the dynamics of particle assembly processes?[6] Because of this lack of understanding, nanostructure growth cannot be predicted; it can only be analyzed after-the-fact. **To fill this major gap in the science of synthesis and build quantitative kinetic models that make atom- and energy-efficient synthesis of these materials a reality, in situ data reporting on the dynamics of these non-classical processes—rather than just the outcomes—are required.** Recently developed in situ transmission electron microscopy (TEM) possesses the spatial and temporal resolution needed to capture the formative events that occur during nucleation and growth of nanostructures. In addition, modern atomic force microscopy (AFM) is capable of directly measuring the interaction energies between interfaces that drive assembly and thus investigating the structure of the interfacial layers that impede it. In this project, these techniques will be used to develop a predictive understanding of particle interactions directed by the surface-coating materials, such as biomolecules and organic ligands.

This work will provide a mechanistic understanding of the energetics and dynamics involved in particle assembly, and thus, the fundamental principles that must be understood to design complex structures with desired properties. Achieving "… *atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties*…." through an understanding of the molecular-to-mesoscale principles controlling the emergence of hierarchical organization addresses both BES's Grand Science Challenges and goals for Mesoscale Science. The success of this project will lead to "… *design, discover, and synthesize new materials and molecular assemblies through atomic-scale control*."

2.0 Research Design and Methodology

2.1 Hypothesis and Objectives

The **hypothetical basis** for this work is that specific short- and long-range interactions between crystals coated with organic ligands or biomolecules are determined by the interfacial structures of solvent/ligand (biomolecule)/crystal surface, leading to the unique nature of biomolecule (ligand)-tethered crystal self-assembly. Therefore, interactions at the crystal surface can be controlled by varying the density of biomolecules on the crystal surface, functional groups of biomolecules (-COOH, -NH_2, and phenyl), the arrangements of functional groups (sequenced-defined peptides and peptoids), ligand length, and solvents. The primary systems that will be studied are metal oxides, such as titanium dioxide (TiO_2), because of their wide application in energy storage. Previous work demonstrates that biomolecules with functional groups of -COOH and -NH_2, such as aspartic acid, thiourea, and serine, affect TiO_2 structures and phases.[2, 7] Metal systems, such as silver (Ag) and gold (Au), also will be employed as model systems to reveal fundamental mechanisms, which then can be extended to oxide systems. The advantage of organic ligands is that the ligand length, which determines the particle separation and interaction forces, can be easily controlled by varying the number of carbons in the ligands. The advantage of biomolecules (e.g., sequence-defined peptides and peptoids) is that sequence-defined molecules with functional sidechains can determine the binding between crystal surfaces and biomolecules, guide interfacial structures of solvent/coating material/crystal surface, direct interactions between particles, and thus create crystal architectures with desired properties. The specific objectives are:

Objective 1. To reveal interfacial structures between crystal surfaces and coating materials (biomolecules and organic ligands) in solvents and the factors that control them, such as ligand length, functional groups in sequence-defined peptides or peptoids (-COOH, -NH_2, and phenyl groups), and solvents (aqueous and organic solvents).

Objective 2. To investigate the interaction forces between crystal surfaces (e.g., van der Waals force, steric hindrance force, and electrostatic force) and their correlation with the interfacial structures.

Objective 3. To discover the dynamics and kinetics of interactions between particle surfaces and their correlations with the interfacial structures.

2.2 Approach

In situ AFM three-dimensional fast force mapping (3D-FFM) technique was used to probe the three-dimensional interfacial structures of solvent/coating material/crystal surface. Theories/simulations, such as molecular dynamics and density functional theory, combined with experiments will reveal the structures of organic-inorganic hybrid surfaces. The interfacial structures will be studied with various ligand lengths, functional groups (-COOH, -NH_2, and phenyl in sequence-defined peptides or peptoids), and solvents (aqueous and organic solvents).

In situ AFM dynamic force spectroscopy (AFM-DFS) was be used to directly measure the interaction energy/force between crystal surfaces at various conditions in objective 1. Molecular dynamics and density functional theory simulations, combined with TEM and AFM results, will confirm the interaction energies/forces and their correlation with interfacial structures directed by surface-coating materials.

In situ TEM will be used to investigate the dynamics and kinetics of particle interactions at conditions corresponding to those used in objective 1. Theories and experimental approaches, such as Derjaguin, Landau, Vervey, and Overbeek theory and Langevin dynamics, will reveal correlations between the molecular nature of biomolecules and interactions (and dynamics) of bio-inorganic hybrid surfaces.

This approach (Figure 1) links the real-time investigation of dynamics to direct measurement of interaction forces and hydration structure to gain an understanding of the role of surface-coating materials (ligands and biomolecules) and reveal the physical controls in particle assembly processes.

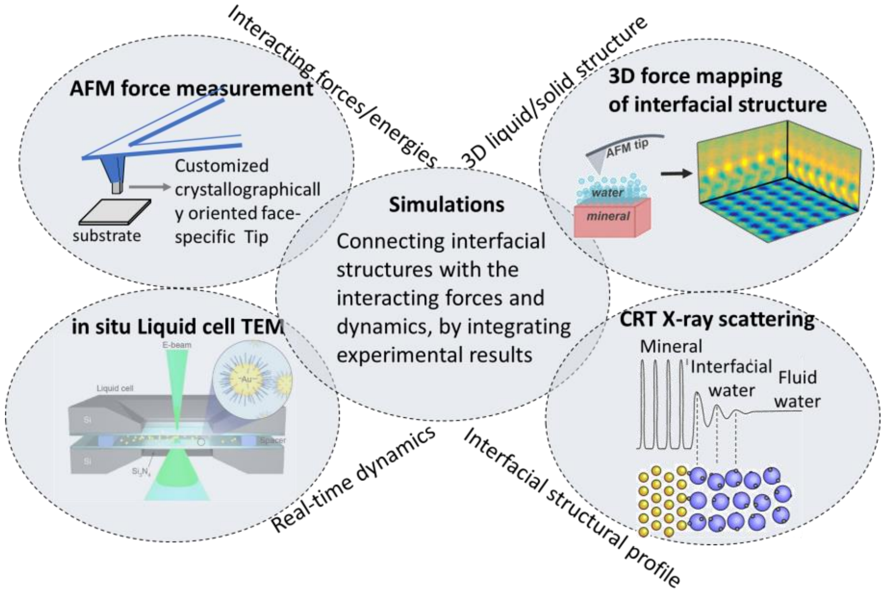

Figure 1. Our research pursues a make-measure-model approach to developing a predictive understanding of synthesis focused on hierarchical structures formed via non-classical pathways of nucleation and growth. We integrate theoretical and experimental methods to span length scales from atomistic to macroscopic.

3.0 Results

3.1 Liquid-Solid Interfacial Structures

TiO_2 was chosen for the study of crystal surface interactions during the OA process leading to branched TiO_2 nanowire growth. As control experiments, we first studied the liquid-solid interfacial structure without peptoids.

3.1.1 Probing 3D Interfacial Structure of Rutile/Water via AFM 3D-FFM

Because the surface Ti atoms are under-saturated 4-coordinated, in contact with water, the surface will be stabilized by chemisorption and physisorption of water. Dissociative adsorption is expected, in which adsorbed H_2O dissociates and interacts with neighboring terminal oxygens to form two hydroxyls. To investigate the surface structure, we directly imaged the TiO_2 surface in water using high-resolution AFM. For (001) surface, a high-resolution AFM (HRAFM) image shows a well-defined lattice structure, with prominent fringes of 3.3 Å being consistent with the d-spacing of the rutile (110) plane. Similarly, the HRAFM image of (100) surface shows vertical lattice fringes of ~ 4.6Å in consistence with the d-spacing of rutile (010) plane and horizontal lattice fringes of ~2.3 Å, which is slightly lower than the d-spacing (2.959Å) of rutile (001) plane due to the sample drift during scanning. These consistent lattice fringes observed in AFM imaging with the Ti atomic structures for both (001) and (100) surfaces demonstrate that the interfacial structure of TiO_2/water is directed by the crystal surface atomic structure. The 3D-FFM images show the side view of the interfacial structure of TiO_2/water, and the force gradient mapping demonstrates that vertical features dissipate beyond ∼1 nm from the surface (Figure 2 C and F), indicating that the absorbed water or dissociated water is roughly 1 nm from the surface under the assumption that the force gradient is from the hydration force induced by the absorbed water on the TiO_2 surfaces.

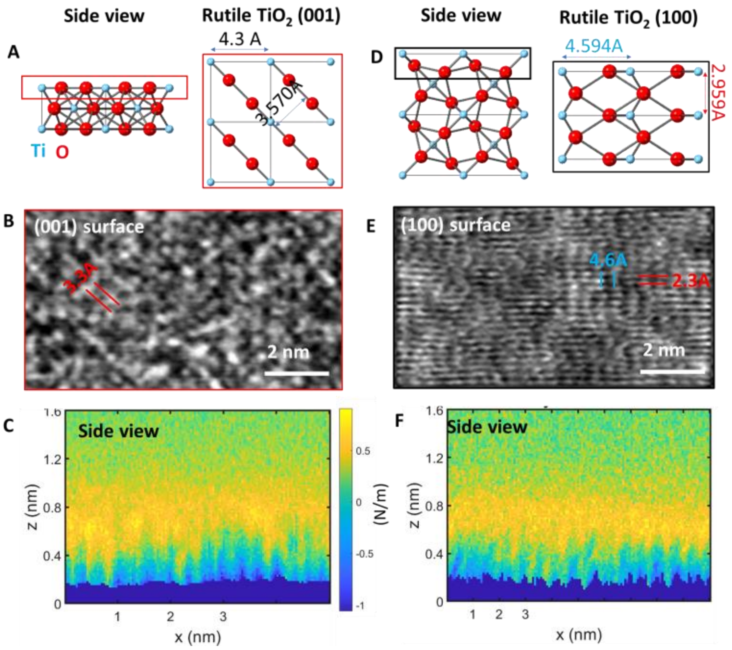

Figure 2. Liquid-solid interfacial structures of rutile (001) and (100) surfaces. A and D, Atomic structures of side and top views of rutile (001) and (100) surfaces, respectively. B and E, AFM images of rutile (001) and (100) surfaces in water, respectively. C and F, FFM images of the side views of rutile (001) and (100) surfaces in water, respectively.

3.1.2 Reconstruction of Molecular Interfacial Structure of Rutile/Water via Classical MD Simulations

We employed classical MD to simulate the molecular structures (Figure 3) of the interface of rutile/water. The water structures obtained from the MD simulations (Figure 3 B and D) show excellent agreement with AFM measurements (Figure 2 B and E). For the (001) surfaces, the top views of the layers of water that are immediately adjacent to the surfaces from the simulation (Figure 3 B) and AFM measurements (Figure 2 B) consistently show a 3.3 × 3.3 Å2-square pattern distribution aligned with the [110] direction of rutile. We note that this is the same pattern followed by the first two layers of surface Ti when viewed from the top (Figure 3 A and B). Similarly, the (100) surfaces also show surface waters following the pattern of surface Ti atoms.

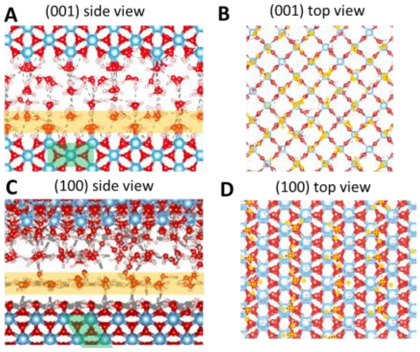

Figure 3 Molecular structures of liquid-solid interfaces of rutile (001)/water (A and B) and (100)/water (C and D) obtained via classical MD simulations.

3.1.3 Characterization of Surface Structure via surface X-ray scattering

To relate the interaction of TiO_2 surfaces with water to their surface structure observed in an aqueous environment, we performed surface X-ray scattering measurements on single crystals of (001) and (100) surfaces in water. The decrease in reflectivity near the anti-Bragg condition of both (00L) and (10L) crystal truncate rods for TiO_2 (001) surface (red solid square in Figure 4 A and B) indicates the increase in roughness in contrast to (100) surface. This result seems consistent with MD simulation results that (100) surface seems smoother (highlighted in yellow in Figure 3A and C). In addition, the extra peak between (001) and (002) (Figure 4A) indicates that the surface absorption results in a new surface rod.

To verify the experimental findings, DFT provides more accurate simulations than MD. Therefore, we plan to conduct DFT to simulate the molecular structure of rutile/water interfaces and verify the interaction of TiO_2 with water.

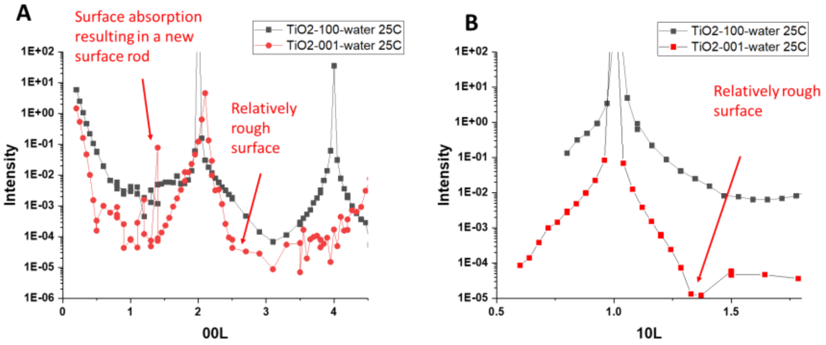

Figure 4. (00L) and (10L) rods for (001) and (100) rutile TiO_2 surfaces in water. A, (00L) rod. B, (10L) rod.

3.2 Crystal Surface Interactions

3.2.1 AFM Tip fabrication

We fabricated customized AFM “crystal tips” with specific surface planes for use as force probes.[8] ~150 x 150 nm TiO_2 pillars that were ~5 μm long were obtained via focused ion beam (FIB) cutting and then mounted to AFM cantilever tips via FIB Pt deposition (**Error! Reference source not found.** 4B). The a ngle between the TiO_2 pillar and the cantilever was controlled to be 10° ±1°.

3.2.2 Probing Interacting Forces between two Crystal Surfaces via AFM-DFS

To investigate the interaction between crystal surfaces, we directly probed the forces between TiO_2 crystal facets via AFM-DFS using an AFM equipped with a rotation stage (Figure 5A). A crystallographically oriented rutile crystal was mounted on an AFM cantilever (Figure 5B) with the rutile (001) or (100) face exposed. During DFS measurements, as the substrate approached the surface, an increasing attractive force between the substrate and probe caused the probe to jump to contact with the substrate (the circled area in Figure 5C). When the tip was retracted from the surface (the purple line), a hysteresis was observed due to strong adhesive forces (F_{ad}) between the substrate and the probe. The tip jumps off from the substrate when this adhesive force was overcome, and the rupture force (F_{ad}) could be measured.

For rutile TiO_2 (001) surface interactions, except a 90° periodic oscillation with respect to rotation angle (θ) as we previously observed[9], the F_{ad} also displayed a 30^{o} periodicity (Figure. 5D), which was not obvious or discussed in detail in our previous work. This 90° periodicity is consistent with a fourfold symmetry of the surface Ti atomic structure (Figure 2A). We propose that the 30^{o} periodicity is attributed to the liquid/solid interfacial structure of TiO_2/water.

For rutile TiO_2 (100) surface interactions, the F_{ad} displayed a 180^{o} periodicity (Figure 5E), in which there is a mirror symmetry by 90^{o} mismatch angle, consistent with a twofold symmetry of the (100) surface Ti atomic structure (Figure 2D).

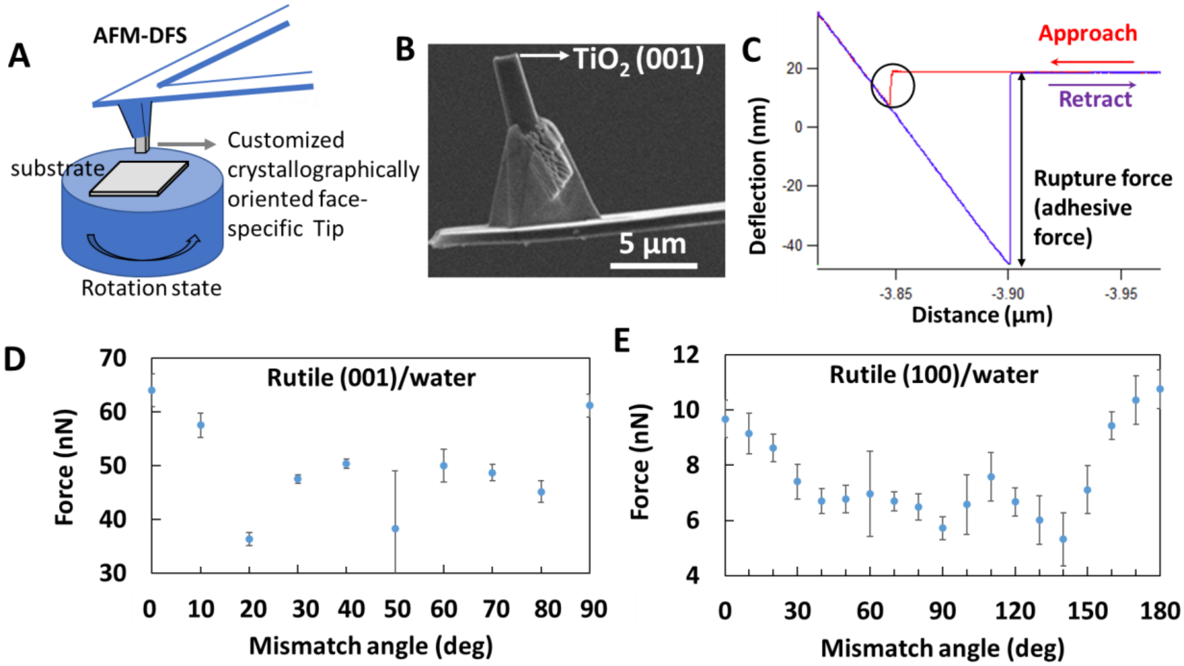

Figure 5. Crystallographic orientation dependence of interacting forces between two crystal surfaces. A. AFM-DFS experimental setup for measuring interacting forces between two crystal surfaces. B. SEM image of a single rutile crystal attached to an AFM cantilever with (001) facet as the probing surface. C. a typical force curve for AFM-DFS measurement. D and E. The force was measured as a function of mismatch angle for rutile (001)/(001) and (100)/(100) surfaces, respectively, at a loading rate of 100 nm/s.

3.2.3 Analysis of Interacting Forces via Classical MD simulations

We applied classical MD to simulate the AFM tip retraction for both (001)/(001) and (100)/(100) surfaces with different mismatch orientations, corresponding to the experimental measurements. We sample angles every 15° from 0° to 180° (only 0-90° is calculated for (001)/(001) surfaces as it has two-fold symmetry within 0-180°), where for each angle we sample separations every 0.5 Å from 8 to 12 Å. The atomic trajectories are recorded and the retraction force is directly calculated for each separation. The results are roughly consistent with experimental results that the F_{ad} displayed a 90° periodicity and a 30^{o} oscillation for the (001) surface and a 180^{o} periodicity for the (100) surface with respect to rotation angle.

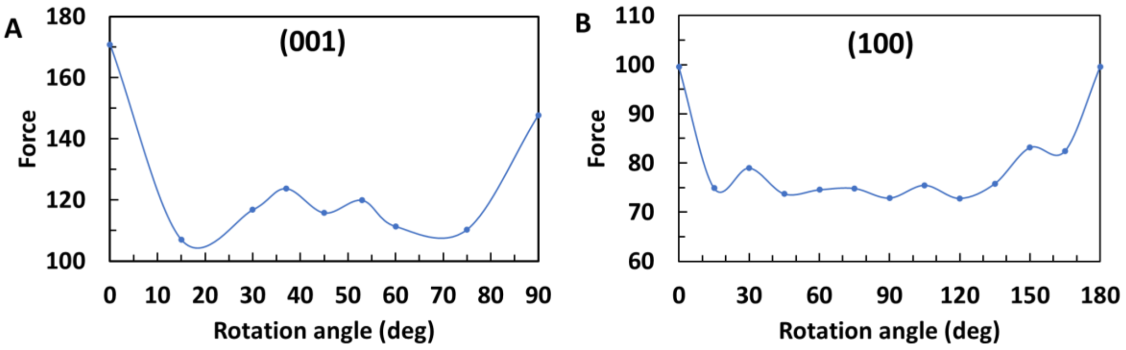

Figure 6. Calculated interacting forces between (001)/(001) and (100)/(100) crystal surfaces in water, showing crystallographic orientation dependence. The force unit is an arbitrary unit.

The classical MD is a powerful atomistic modeling approach suitable for modeling systems with thousands to millions of atoms. Previous studies have developed force fields that allow classical MD to reproduce the lattice structure of rutile with excellent accuracy. However, the intrinsic drawback of the force fields requiring a finite cutoff introduces artificial effects when calculating electrostatic potentials, leading to unphysical Coulomb interactions. Consequently, all force predictions are not accurate, potentially yielding inaccurate interfacial water structures.

3.3 Future work

Although the simulation results are consistent with experimental ones, we plan to continue to investigate the rutile/water interface using *ab initio* MD based on density functional theory (DFT) which can accurately capture the electronic effects. However, the high computation cost of DFT calculations requires the modeling system to be small enough for a practical simulation time. Therefore, further investigation of finite size effects is needed to complement the study.

We will coat the crystal surface with biomolecules and organic ligands and use the similar approach that we employed for the control experiments (rutile/water system) to reveal interfacial structures between crystal surfaces and coating materials in solvents and the factors that control them, such as ligand length, functional groups in sequence-defined peptides or peptoids (-COOH, $-NH_2$, and phenyl groups), and solvents (aqueous and organic solvents).

We will conduct in situ TEM to investigate the dynamics and kinetics of particle interactions at various conditions mentioned above.

4.0 References

1. Wang, Y.; Wan, D.; Xie, S.; Xia, X.; Huang, C. Z.; Xia, Y., Synthesis of Silver Octahedra with Controlled Sizes and Optical Properties via Seed-Mediated Growth. *Acs Nano* **2013,** *7* (5), 4586-4594.
2. Li, D.; Soberanis, F.; Fu, J.; Hou, W.; Wu, J.; Kisailus, D., Growth Mechanism of Highly Branched Titanium Dioxide Nanowires via Oriented Attachment. *Crystal Growth & Design* **2013,** *13* (2), 422-428.
3. Xia, Y.; Gates, B.; Li, Z.-Y., Self-Assembly Approaches to Three-Dimensional Photonic Crystals. *Advanced Materials* **2001,** *13* (6), 409-413.
4. Chaudhary, V.; Sharma, S., An overview of ordered mesoporous material SBA-15: synthesis, functionalization and application in oxidation reactions. *Journal of Porous Materials* **2017,** *24* (3), 741-749.
5. Nudelman, F.; Gotliv, B. A.; Addadi, L.; Weiner, S., Mollusk shell formation: mapping the distribution of organic matrix components underlying a single aragonitic tablet in nacre. *Journal of structural biology* **2006,** *153* (2), 176-187.
6. Yan, F.; Liu, L.; Walsh, T. R.; Gong, Y.; El-Khoury, P. Z.; Zhang, Y.; Zhu, Z.; De Yoreo, J. J.; Engelhard, M. H.; Zhang, X.; Chen, C.-L., Controlled synthesis of highly-branched plasmonic gold nanoparticles through peptoid engineering. *Nature Communications* **2018,** *9* (1), 2327.
7. Ren, P.; Song, M.; Lee, J.; Zheng, J.; Lu, Z.; Engelhard, M.; Yang, X.; Li, X.; Kisailus, D.; Li, D., Edge Dislocations Induce Improved Photocatalytic Efficiency of Colored TiO2. *Advanced Materials Interfaces* **2019,** *6* (17), 1901121.
8. Wu, Z.; Chun, J.; Chatterjee, S.; Li, D., Fabrication of oriented crystals as force measurement tips via focused ion beam and microlithography methods. *Surf. Interface Anal.* **2018,** *50* (1), 117-122.
9. Li, D.; Wang, H.; Xiao, D.; Song, M.; Legg, B.; Chun, J., Investigating the magnitude and source of orientation-dependent interactions between TiO 2 crystal surfaces. *Nanoscale* **2017,** *9* (29), 10173-10177.

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