Supporting Information

Oriented Attachment: From Natural Crystal Growth to a Materials Engineering Tool

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**S1: Oriented attachment as an alternative crystal growth process in aqueous solvents**

*General:* Oriented attachment of charge-stabilized crystals in aqueous solvents is of interest in the research on biominerals, geology, materials science, and of course for crystallography itself. A selection of reports from this millennium are presented in the supplementary information, Table S1 and Table S2. Commonly, crystal growth by oriented attachment is coined non-classical crystal growth\(^1\), to distinguish it from the classical atom-by-atom (molecule-by-molecule) growth of crystals. Oriented attachment between crystals is observed in natural biological conditions and is assumed to be important for biomineral formation.\(^1-4\) Oriented attachment of hydroxyapatite (Ca\(_5\)(PO\(_4\))\(_3\)(OH)) and calcium carbonate (CaCO\(_3\)) crystals has been studied to understand bone formation and bio-skeletons. Analytical studies of oriented attachment are partially impeded by the existence of a plethora of crystal polymorphs for these compounds. For relatively stable crystals consisting of for example TiO\(_2\), SnO\(_2\), magnetite, hematite, and ZnO, the crystal formation by oriented attachment is enhanced by so called “hydrothermal coarsening”, which means high temperatures and pressures applied in an autoclave.\(^5-9\) Crystals of Fe-oxide compounds (magnetite, hematite) are of interest from a geological perspective and magnetism as well.

The common scientific questions are related to the driving force for oriented attachment, the type of crystallographic facets involved, the precise mechanism on an atomic scale, the origin of defects in crystals such as twinning planes, edge- and screw dislocations.\(^1\) In a minority of cases the crystals formed by oriented attachment under hydrothermal aging are considered as building blocks of technological interest, for instance in opto-electronics (solar cells).\(^10,11\)

*Driving forces and facet specificity:* Sols in water are stable due to the electrical double layer around the crystals; with one type of charges on the crystal surface counteracted by a diffuse layer of countercharge. Regarding the facet specificity, one can imagine that the density of
charges on the crystals can depend on the chemical surface termination of specific facets. For a number of crystals, the surface energy or crystal/liquid interfacial energy per unit area is understood to a certain extent; in reports one finds the notions of higher – and lower -energy surfaces.\textsuperscript{10, 12-14} The energy lowered by crystal attachment will be strongest if two high-energy facets are eliminated by connection. Often, strong adsorption of H\textsubscript{2}O to specific facets can be a factor that decides which facets are involved in the epitaxial connection between crystals during hydrothermal coarsening. Frequently oriented attachment between charge-stabilized crystals has been observed when the temperature is raised above room temperature, described in the literature as \textit{hydrothermal treatment}\textsuperscript{2, 9, 12, 13, 15-17}; this means that Brownian motion of the dispersed crystals becomes so vivid that the protecting charge double layer breaks up in a collision, and facets face each other on a short distance. The increase of oriented attachment by raising the temperature is thus mostly a kinetic effect.

One of the best studied cases is oriented attachment of anatase TiO\textsubscript{2} nanocrystals. Penn et al.\textsuperscript{12} reported oriented attachment via the high energy (001) and (112) facets. Adachi et al.\textsuperscript{10} showed that these facets can be blocked by certain ligands, and that oriented attachment then occurs via lower energy facets. During hydrothermal coarsening it is often found that nanocrystals attach to form rods, mostly with the polar facets involved. In a second stage these rods adhere along their long direction and finally attach to form sheets or 3D materials, either fully closed or with pores present. Hierarchical construction of porous materials for opto-electronic applications and energy storage is an interesting engineering pathway, provided that the building blocks as well as the facet selectivity in the attachment can be precisely controlled.

The study of crystal defects and annealing of crystal defects: Crystal defects originating from imperfect oriented attachment have been studied by ex-situ high resolution transmission electron microscopy (HRTEM). An early study of TiO\textsubscript{2} showed that twinning planes in a crystal, and edge and screw dislocations can be caused by imperfect oriented attachment.\textsuperscript{12, 18}
The presence crystal defects constituted the first strong indication that oriented attachment is a prominent mechanism of crystal growth, abundant in natural and laboratory conditions. Twinning can occur when identical crystallographic facets face each other and attach, sharing the same crystal lattice points between them. An edge dislocation results from an atomic plane that ends halfway between the two planes that connect; a screw dislocation is more intricate to understand. Later on, the annealing of defects has been monitored in time under two types of conditions: (i) in the vacuum and beam conditions of an electron microscope\textsuperscript{19}, (ii) with special samples containing ultra-thin films of nanocrystals and the liquid medium\textsuperscript{20-22}. 
Table S1. Overview of reports on oriented attachment of charge-stabilized crystals in water or polar solvents

| Compound | Reference | Building blocks | Solvent, ligands (7), and experimental conditions | Type of crystals formed by oriented attachment | Scientific interest | Application |
|----------|-----------|----------------|-----------------------------------------------|-----------------------------------------------|-------------------|-------------|
| TiO₂     | 18        | Anatase nanocrystals, - multi-faceted - 5 nm - active facets: high energy facets (112), (001) | Water, hydrothermal coarsening | Larger crystals formed from two or more nanocrystals | Understanding the formation of edge- and screw dislocations formed by imperfect oriented attachment | Fundamental knowledge |
| TiO₂     | 12        | Preformed nanocrystals - anatase, brookite - multi-faceted - 5 nm - active (112) and (001) facets | Water, hydrothermal coarsening | Larger crystals with epitaxial connections and twinned interfaces | Understanding twinning and polytypism in crystal growth | Fundamental knowledge |
| TiO₂     | 10        | Preformed anatase nanocrystals - few nm in size - high energy (001) facet covered with surfactants, (101) active | Polar solvent | Anatase nanowires along the <101> direction by (101) facet attachment, different from Penn et al. | Understanding the type of facets used in oriented attachment | Assemblies of attached TiO₂ rods as high-surface area material for dye-sensitized solar cells |
| TiO₂     | 7         | Ti(IV)/Oxides → fibers → branched rutile microcrystals via oriented attachment | Acidic water | Rutile fibers with c-axis as long axis - more complex and larger crystals with attachment via the lateral (110) facets | Hierarchical assembly and oriented attachment on different stages of the hydrothermal coarsening | -- |
| TiO₂     | 23        | TiO₂ nanocrystals, anatase, charge-stabilized in water | Water and salts | Larger crystals with attachment via (112) facets, and (001) and (100) facets: single crystals and twinned crystals | Understanding facet-selectivity in OA of anatase NCs, charge-stabilized: attractive interactions between double layers, water molecules on facets can prevent OA | -- |
| TiO₂     | 24        | Synthesis in autoclave starting from Ti-isopropanoxide, trimethyl ammonium hydroxide resulting in TiO₂ nanocrystals, anatase, (001) high energy facets | Autoclave, water, 250 °C | Anatase nanorods along <001>, attachment via high-energy (001) facets - further ripening to ellipsoids | -- | Anode material for Na-ion battery |
| TiO₂     | 25        | TiCl₄ and H₂O | Atomic layer deposition on a graphene crystal, 300 °C | Anatase rods and V-shaped structures in alignment with underlying graphene crystal | Understanding non-typical ALD growth: formation of small flat NCs that move along the surface, coalescence, restructuring and rod crystallization | -- |
| TiO₂     | 26        | Ti(IV) complex and water | Water, hydrothermal. Coarsening | Primary 6 nm elongated NCs with <001> as long direction - spindle-like large structures (500 nm) with pores formed by oriented attachment of primary NCs along (001) direction and sides ways | Understanding hierarchical growth | Anode material for Na-ion battery |
| SnO₂     | 13        | Preformed SnO₂ nanocrystals: - nearly spherical, 1-2 nm, multi-faceted - charge stabilized - 100 facets lowest in energy | Water, coagulation at isoelectric point | Disordered rods of a few attached nanocrystals | Understanding the effect of Brownian motion vs. nanocrystal alignment by facet/facet interactions | -- |
| SnO₂     | 27        | SnCl₂ in water/ethanol mixture | Water/ethanol | Disordered sheets, rutile, non-stoichiometric | Understanding sheet formation in one pot-synthesis, small NCs as intermediates | Li battery |
| SnO₂     | 28        | Sn(citrate) and manganese(citrate), heating up to 500 °C results in NCs, truncated octahedrons | Nanocrystals formed in polar solvent, oriented attachment performed under dry conditions at 700 °C | 2D-3D disordered agglomerates, Mn²⁺ ions at facets impede or slow down oriented attachment | HR TEM study of facet/facet connections in NC clusters with strong misalignment | -- |
| Compound                        | Reference | Building blocks | Solvent, ligands (?) and experimental conditions | Type of crystals formed by oriented attachment | Scientific interest | Application                      |
|--------------------------------|-----------|----------------|------------------------------------------------|-----------------------------------------------|---------------------|----------------------------------|
| SnO₂                           | 29        | - NCs in water - 5 nm | Basic water, coarsening for several days | - Nanocrystals attach to wires <112> direction - Wires attach via their sizes to sheets and 3D crystals | - Understanding of hierarchical steps in crystal formation - Understanding oriented attachment on several stages | --                          |
| SnO₂                           | 14        | - SnCl₂ in water at very high pressure → elongated monodisperse dodecahedrons 200 nm, - active (100), (110) facets in O₃, (111) facets protected by NMe₃ | Water, autoclave, 220 °C, very high pressure | 3D very well-ordered structures, with attachment mostly via (100) facets | - Understanding crystal growth under high pressure - Understanding assembly of large monodisperse crystals into ordered superstructures under high pressure | --                          |
| CaCO₃                          | 30        | Ca(Cl₂), NH₄Cl, CO₂ in water | --                                              | Ca²⁺ ions → amorphous CaCO₃ → vaterite (190) terminated sheets (>100nm) stabilized with NH₄ → stacks → 3-D calcite by OA | Biomimeralization via intermediate steps in which OA is important | --                          |
| CaCO₃                          | 3         | Ca(OH)₂ + CO₂ → 3b-50 nm truncated nanocubes, with (100) facets | Water, room temperature | Linear structures and multi-branched 2D and 3D aggregates by OA of the nanocubes | Understanding interaction between charged facets (Ca²⁺, CO₃²⁻ terminated) in biomimeralization | --                          |
| CaCO₃                          | 31        | Rod-like structures formed from NCs (see above) | Water | Lateral attachment of rods forming bundles | Attachment directed by surface charge | --                          |
| Ca₃(PO₄)₂(OH)₂, hydroxyapatite | 2        | Amorphous particles and nanocrystals | Water, hydrothermal aging | - Wurtzite nanorods along polar c-axis, 5 nm in diameter, 20-100 nm in length - Assemblies of oriented nanorods | Understanding bone formation with biomimetic experiments | --                          |
| Fe₃O₄ (magnetite)              | 32        | Preformed 5 nm Fe₃O₄ nanocrystals | Polar solvent | Large porous spheres 100 nm in diameter formed by OA of 5 nm crystals | Understanding oriented attachment | --                          |
| Fe₃O₄ (hematite)               | 33        | 100 nm hematite nanocrystals, with facets | Water, hydrothermal | | Understanding oriented attachment of large crystals in water - Interplay of facet-specific interactions and magnetic dipoles | Formation of magnetic materials |
| Fe₃O₄ (tet- and a-phase)       | 34        | Fe(NO₃)₃ in water(NH₄)H₂PO₄ | Hydrothermal reaction at 200 °C in autoclave | - Primary nanocrystals; e-Fe₃O₄ 10-15 nm in size - Formation of nanoflakes and ellipsoid-shaped structures, 200-500 nm in size with a-crystal structure, formed by OA | Formation of e-Fe₃O₄ nanocrystals with beneficial magnetic properties - Slow decay of this phase to large aggregates of Fe₃O₄ with smaller coercitivity | --                          |
| Fe₃O₄(OH)₂, goethite           | 35        | Fe(OH)₃ in water = O₂ | Water | - Nanorode by isotropic crystal growth - OA of rods via lateral (110) facets to larger crystalline rods (30 nm in width, 200 nm in length) | Understanding the formation of Goethite rods via a hierarchical process | --                          |
| ZnO                            | 36        | Ligand-free NCs, 5 nm in size | Polar solvent aging of the NCs in MeOH/chloroform | Monodisperse nano-porous ellipsoids, about 200 nm in length, 100 nm in width, 8 nm pores | Proof that mesoscopic 3D systems can be formed by OA in polar solvents | Photocatalysis photo degradation of organic waste |
| ZnO                            | 37        | One-pot synthesis, based on Zn(acetate), in ethanol, NCs are intermediates in rod formation | Water/Ethanol | Hydrothermal coarsening in autoclave | Oriented attachment on diverse hierarchical moments in the wurtzite formation, during formation of 7 nm crystals, which then form (15,100 nm) wurtzite rods Axial oriented attachment of small nanocrystals vs. lateral attachment | --                          |
| Compound | Reference | Building blocks | Solvent, ligands (7), and experimental conditions | Type of crystals formed by oriented attachment | Scientific interest | Application |
|----------|-----------|----------------|-----------------------------------------------|-----------------------------------------------|-------------------|------------|
| ZnO | 9 | One pot synthesis based on hydrolysis of Zn(OH)\_2 under hydrothermal conditions, ZnO NCs as intermediate phase | Water, sodium dodecyl sulfonate as ligand, presumable adsorbed at the lateral facets of the wires | ZnO nanowires along <0001> wurtzite axis, 20-80 µm, 50-200 nm diameter | Role of sodium dodecyl sulfonate ligands adsorbing at the lateral (100) facets, promoting stronger anisotropy | Opto-electronic devices, sensitive UV photodetector |
| ZnO | 38 | Measurement of (0001) facet-to-facet forces by AFM | Water | -- | Understanding facet-to-facet forces as a function of distance (intervening water layers) and relative in-plane angle | -- |
| BaTiO\_3 | 39 | Multi-facetted BaTiO\_3 NCs in water, cubic NCs in organic solvent, oleic acid capped | Water, hydrothermal - Organic solvents | Systems with a few nanocrystals attached, with alignment of the nanocrystals | Model study based on results of two other reports, competition between van der Waals facet/facet interactions, and assembly directed by the NC dipole moment around the c-axis | -- |
| MnS | 40 | Manganese (Mn-C) and elemental sulfur | Dry mixture, autoclave, 500-800 °C | Porous mesoporous carbon/MnS architectures by oriented attachment of MnS 200-400 nm crystals in the carbon support | -- | Anode material for Li batteries |
| Mn\(_2\)O\_3 | 41 | Structures with interconnected MnO\_6 octahedra forming linear pores | Monitoring oriented attachment of the building blocks in a liquid cell | - primary building blocks attach - finally a nanowire with several pore-channels is formed | Peculiar crystal structures with molecular-like binding mechanisms | -- |
| Mn\(_2\)O\_3, MnO\_2 | 42 | Interconnected MnO\_6 octaheders form hexagonal nanoflakes along a <100> direction | Water | Nano flakes attach in imperfect way to form multi-domain nanoflower structures | Understanding edge-to-edge oriented attachment of nanoflakes promoted by hydrogen bonds | -- |
| CoO | 43 | Co\(_2\)O\_3 forms CoO nanorods in solvothermal conditions | Water | - Rods attach side-by-side to plates - Plates attach to form book-like structures | Understanding hierarchical OA using several facet types | Energy storage in super-capacitors |
| Au | 44 | Au NCs dispersed | Water, laser-light in the near IR | Hierarchical oriented attachment - NCs attach to form rods, - rods attach in length and laterally - longer rods attach to form micron sized wires | Understanding hierarchical OA, driven by heating and plasmon resonances | -- |
| Au | 45 | Citrate-stabilized Au nanocrystals, 2 nm in size, multi-faceted | Water, liquid cell | NC dimers attached via (111) facets | In-situ study of rotational motion of nanocrystals, and finally epitaxial connection | -- |
| PbSe | 46 | Pb(CH\_3COO)\_2 and Na\(_2\)SeO\_3 Chemical bath deposition of a GaAs wafer | Water at pH = 13 | Small cubic PbSe nanocrystals formed in solution, attach via (100)(100) interactions to columns | Preparing electronic grade and quantized thin PbSe films | -- |
| PbTiO\_3 perovskite fibers | 17 | Pb(NO\_3)\_2 and Ti(OH)\_4 | Water, hydrothermal conditions | PbTiO\_3 nanorods that evolve into ribbons with diameters of 250 nm via lateral OA, using (110) planes | Formation of high-quality crystalline ribbons, photoluminescence in visible region | -- |
| Compound | Reference | Building blocks | Suspension, ligand, method | Crystal formed by oriented attachment | Scientific interest | Application |
|----------|-----------|----------------|---------------------------|---------------------------------------|---------------------|-------------|
| PbSe     | 47        | Nanocrystals - rock salt - truncated cube - octahedron - few nm - (100) or (110) or (111) depending on ligands | Organic, ligand-stabilized nanocrystals | - Direct synthesis of straight nanowires along <100> - 4-20 nm diameter, micrometre length - Nanocrystals by oriented attachment of nanocrystals with use of: (100) facets (oleates), (110) facets (amines) (111) facets (hexadecylamine) | Study of active facet selectivity depending on the ligand stabilization, strong anisotropy with centrosymmetric crystal structure | Opto-electronic materials |
| PbSe     | 48        | - One-pot synthesis with Pb- and Se-precursors - 5 nm PbSe nanocube intermediates | Organic | - PbSe nanowires formed by O`A attachment of 5 nm nanocrystal intermediates aligned along a <100> direction - Liquid crystals of aligned nanorods | - study of anisotropic crystal growth with centrosymmetric rock salt crystal structure | Opto-electronics |
| PbS      | 49        | - One-pot synthesis, PbS nanocrystals as intermediates, dense packing of oleates on (100) planes | Organic, CI-containing co-solvent | - Extended (µm) 2D sheets, 5 nm in thickness, OA attachment of nanocrystals, presumably along the (110) direction | - formation of 2D opto-electronic materials by wet chemistry | Opto-electronics |
| Mn₃O₄    | 50        | - Autoclave synthesis in water of 20-30 nm truncated cuboids - 6 (100) facets - oleic acid capped | Hexane and toluene, solvent evaporation, NC assembly at liquid/air interface, heating | - Linear rods <100> direction, with epitaxial connection via the (100) facets - Square monolayers with attachment at 4 (100) facets | - Understanding assembly of capped nanocubes at organic liquid/air interface, OA upon removal of oleic acid | -- |
| ZnS      | 51        | Nanocrystals - zinc blende - multi-faceted - 5 nm | Organic solvents, oleic acid, hexadecylamine | - Direct synthesis of nanorods of 5nm diameter, 20 nm length - Oriented attachment of nanocrystals to rods | Facet-selective oriented attachment | Opto-electronic materials |
| CdSe     | 52        | Direct one-pot synthesis, nanocrystals as intermediates | Organic, alkylamine ligands of different lengths | - Direct synthesis of CdSe nanorods 1.5 – 6nm in diameter, via intermediate phases of pearl-necklace or string-of-pearls agglomerates | Understanding nanowire growth, via intermediate agglomeration, and OA | Opto-electronic materials |
| Au       | 53        | Chloroauric acid and oleylamine (reductor) in a toluene medium | Organic solvents | - Ionic precursors → Au nanocrystals 2 nm in size → Au nanowires with of 2 nm in diameter up to µm, growth along the <111> axis - Arrays of nanowires | - Understanding anisotropic growth by OA of cubic fcc nanocrystals - Formation of twin defects, and atomic reconfigurations, smoothening the nanowires | -- |
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