Supporting Information

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

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Contents

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.[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_2O 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 *hydrothermal treatment*[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_2 nanocrystals. Penn et al.[12] reported oriented attachment via the high energy (001) and (112) facets. Adachi et al.[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_2 showed that twinning planes in a crystal, and edge and screw dislocations can be caused by imperfect oriented attachment.[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[19], (ii) with special samples containing ultra-thin films of nanocrystals and the liquid medium.[20-22]

Table S1. Overview of reports on oriented attachment of charge-stabilized crystals in water or polar solvents

Compound	Reference	Building blocks - crystal structure - shape - size - active facet	Solvent, ligands (?), and experimental conditions	Type of crystals formed by oriented attachment	Scientific interest	Application
TiO_2	18	Anatase nanocrystals, - multi-facetted - 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
TiO_2	12	Preformed nanocrystals - anatase, brookite - multi-facetted - 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
TiO_2	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 TiO_2 rods as high-surface area material for dye-sensitized solar cells
TiO_2	7	Ti(IV)Oxides → fibers → branched rutile meso-crystals 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	--
TiO_2	23	TiO_2 nanocrystals, anatase, charge-stabilized in water Atomistic simulations of attachment	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	--
TiO_2	24	Synthesis in autoclave starting from Ti-isopropoxide, trimethyl ammonium hydroxide resulting in TiO_2 nanocrystals, anatase, (001) high energy facets	Autoclave, water, 230 ºC	- anatase nanorods along <001>, attachment via high-energy (001) facets - further ripening to ellipsoids	--	Anode material for quantum dot-sensitized cells
TiO_2	25	$TiCl_4$ and H_2O	Atomic layer deposition on a graphene crystal, 300 ºC	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	--
TiO_2	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
SnO_2	13	Preformed SnO_2 nanocrystals: - nearly spherical, 1-2 nm, multi-facetted - 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	--
SnO_2	27	$SnCl_2$ in water/ethanol mixture Endured aging at 120 °C	Water/ethanol	Disordered sheets, rutile, non-stoichiometric	Understanding sheet formation in one pot-synthesis, small NCs as intermediates	Li battery
SnO_2	28	$Sn(citrate)_2$ and $manganese(citrate)_2$, 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 agglomorates, Mn^{2+} ions at facets impede or slow down oriented attachment	HR TEM study of facet/facet connections in NC clusters with strong misalignment	--

Table S1. Overview of reports on oriented attachment of charge-stabilized crystals in water or polar solvents (continued)

Compound	Reference	Building blocks - crystal structure - shape - size - active facet	Solvent, ligands (?), and experimental conditions	Type of crystals formed by oriented attachment	Scientific interest	Application
SnO_2	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 via oriented attachment on several stages	--
SnO_2	14	- $SnCl_2$ in water at very high pressure → elongated monodisperse dodecahedrons 200 nm, - active (100), (110) facets in OA, (111) facets protected by NMe_3	Water, autoclave, 220 ºC, 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	--
$CaCO_3$	30	$CaCl_2$, NH_4Cl, CO_2 in water	--	Ca^{2+} ions → amorphous CaCO3 → vaterite (100) terminated sheets (>100nm) stabilized with NH_4^+ → stacks → 3-D calcite by OA	Biomineralization via intermediate steps in which OA is important	--
$CaCO_3$	3	$Ca(OH)_2 + CO_2$ → 30-50 nm truncated nanocubes, with (104) facets	Water, room temperature	Linear structures and multi-branched 2D and 3D aggregates by OA of the nanocubes	Understanding interaction between charged facets (Ca^{2+}, CO_3^{2-} terminated) in biomineralization	--
$CaCO_3$	31	Rod-like structures formed from NCs (see above)	Water	Lateral attachment of rods forming bundles	Attachment directed by surface charge	--
$Ca_5(PO_4)_3(OH)$, 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	--
Fe_3O_4 (magnetite)	32	Preformed 5 nm Fe_3O_4 nanocrystals	Polar solvent	Large porous spheres 100 nm in diameter formed by OA of 5 nm crystals	Understanding oriented attachment	--
Fe_2O_3 (hematite)	33	100 nm hematite nanocrystals, with facets	Water, hydrothermal	- 1D chains and extended hexagonal monolayers and films by OA of 100 nm hematite NCs - OA via (110) planes, while (001) facets have lowest surface energy	- Understanding oriented attachment of large crystals in water - Interplay of facet-specific interactions and magnetic dipoles	Formation of magnetic materials
Fe_2O_3 (e- and a-phase)	34	$Fe(NO_3)_2$ in water/$(NH4)_2HPO_4$,	Hydrothermal reaction at 200 ºC in autoclave	- Primary nanocrystals: e-Fe_2O_3 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-Fe_2O_3 nanocrystals with beneficial magnetic properties - Slow decay of this phase to large aggregates of Fe_2O_3 with smaller coercitivity	--
FeO(OH) goethite	35	$Fe(OH)_2$ in water + O_2	Water	- Nanorods 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 $Zn(acetate)_2$ in ethanol, NCs are intermediates in rod formation	Water/Ethanol Enduring hydrothermal coarsening in autoclave	ZnO nanocrystals 1-3 nm diameter, ZnO nanorods with <0001> wurtzite long axis, 15 nm in diameter, 100 nm in length	Oriented attachment on diverse hierarchical moments in the coarsening, during formation of 7 nm crystals, which then form (15,100 nm) wurtzite rods Axial oriented attachment of small nanocrystals vs. lateral attachment	--

Table S1. Overview of reports on oriented attachment of charge-stabilized crystals in water or polar solvents (continued)

Compound	Reference	Building blocks - crystal structure - shape - size - active facet	Solvent, ligands (?), 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	Manganocene (Mn-C) and elemental sulfur	Dry mixture, autoclave, 500-800 °C	Porous mesoscopic carbon/MnS architectures by oriented attachment of MnS 200-400 nm crystals in the carbon support	--	Anode material for Li batteries
MnO_2	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_2O_3, MnO_2	42	Interconnected MnO_6 octaeders form hexagonal nanoflakes along a <100> direction	Water	Nanoflakes attach in imperfect way to form multi-domain nanoflower structures	Understanding edge-to-edge oriented attachment of nanoflakes promoted by hydrogen bonds	--
CoO	43	$CoCO_3$ 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-facetted	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_2SeO_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	--

Table S2: Overview of reports on oriented attachment in organic non-polar solvents

Compound	**Reference**	**Building blocks** **- crystal structure** **- shape** **- size** **- active facet**	**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 - Nanorods 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 centro-symmetric 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, Cl-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
Mn_3O_4	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 agglomorates	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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