SPECIAL ARTICLE

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Ceramic nanostructures of SnO₂, TiO₂, and ZnO via aqueous crystal growth: cold crystallization and morphology control

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Ceramics are traditionally synthesized using high temperature annealing. However, cold crystallization is studied with respect to energy saving, low environmental impact, low cost, and hybridization with organic materials and metals, etc. In addition, nanostructure control is required for higher functionality. In this paper, crystal growth control in aqueous solution and morphology control of the ceramic nanostructures are introduced to provide next-generation devices.

Key-words: Cold crystallization, Morphology control, Nano-structure, Crystal growth, Aqueous solution

1. Introduction

Ceramics are conventionally synthesized using high temperature annealing. “Cold synthesis”, especially “cold crystallization”, is, since many years an intensely studied topic in the field of ceramics to improve energy saving, low environmental impact, low cost, and hybridization with organic materials and metals, etc. In addition, controlling the nanostructure of ceramics is necessary to improve the performance of electronic and functional devices. In contrast, metal oxides are created in nature at room temperature, atmospheric pressure, and in aqueous solutions. As a result, fine microstructures are formed in plants and animals, proving that nature provides great guidance. This article reviews research into cold crystallization (room temperature crystallization) and morphology control (nanostructure control) of ceramics, while a number of related studies were previously reviewed.1–8)

2. Development of SnO₂ nanostructures

2.1 Development of SnO₂ nanostructures and morphology control

SnO₂ has a tetragonal crystal structure. The a-axis and b-axis have the same crystal axis length, but the c-axis has a different crystal axis length, and a = b ≠ c. Therefore, the crystal morphology can be controlled using anisotropic growth. SnO₂ nanostructures were developed via anisotropic growth and their growth orientations and/or crystal planes discussed.

Liu et al. synthesized urchin-like hollow SnO₂ nanostructures from a hydrothermal solution containing SnSO₄, H₂SO₄, and water.9) Hollow SnO₂ urchins possessed enriched prickles with diameters of 5–20 nm, a length of <70 nm, and a high surface area of up to 116 m² g⁻¹.

Lou et al. reported the template-free hydrothermal synthesis of SnO₂ hollow particles to produce anodes for a lithium-ion battery (Fig. 1).10) Potassium stannate trihydrate (K₂SnO₃·3 H₂O, 4.7–40 mM) was added to an ethanol-H₂O mixture (30 mL, EtOH 25–50 vol%). The solution was kept at 150 °C for a period of 3–48 h after the addition of urea, thiourea, or ethyl diamine to obtain the particles. Interconnected core/shell-type SnO₂ hollow particles with sizes in the range of 150–250 nm and a shell thickness of approximately 30 nm were prepared at 150 °C for 24 h (EtOH: 50 %, K₂SnO₃·3 H₂O: 8.4 mM). They were polycrystalline and the diffraction rings from inside to outside were indexed to the (110), (101), (200), (211), and (112) planes of rutile SnO₂, respectively. The hollow nanospheres had a large initial discharge capacity of 1140 mAh g⁻¹, which was more than 75 % higher than that of pristine SnO₂ nanoparticles (ca. 645 mAh g⁻¹).11)

Wang et al. synthesized yellow flower-like assembled SnO₂ nanosheets via a hydrothermal reaction in a solution containing SnCl₂·2 H₂O (15.8 mM), ethanol, and water (pH ≈ 11) at 120 °C for 6 h (Fig. 2).12) The selected-area electron diffraction (SAED) pattern was indexed as the (110), (101), (200), (211), and (301) planes of rutile-type SnO₂. Three crystal planes were observed to conclude that the crystal planes belonged to the same (110) plane. The assemblies of the sheets had a BET surface area of 180.3 m² g⁻¹.
Pan et al. synthesized SnO$_2$ nanobelts by thermal evaporation of either SnO$_2$ powders at 1350 °C or SnO powders at 1000 °C (Fig. 3). The SnO$_2$ nanobelts had widths in the range of 50 to 200 nm. The cross-sectional areas of the SnO$_2$ nanobelts were rectangular, with width-to-thickness ratios of approximately 5 to 10. Nanobelts were single crystalline and dislocation-free. They grew along [101] and were enclosed by (010) and (10-1) crystallographic facets. SnO$_2$ nanowires, nanoribbons, and nanotubes were synthesized using an elevated temperature synthesis technique. Nanostructures were formed from SnO/Sn- and SnO-based mixtures in a furnace at 1050–1150 °C. The SnO$_2$ nanowires had a rectangular cross section enclosed by ±(010) and ±(10-1) facet planes, and a thickness-to-width aspect ratio ranging from 1:2 to 1:5, which were smaller than those for the SnO$_2$ nanobelts. The growth of these SnO$_2$ nanowires was parallel to the [101] crystal direction.

Zhang et al. fabricated SnO$_2$ nanorods with diameters of approximately 8–15 nm and lengths between 150–200 nm (Fig. 4). Nanorods grew from the center of multi-needle-shaped nanorod particles. They were formed by the reverse micelle hydrothermal process at 200 °C for 18 h in a solution containing SnCl$_4$, NaOH, heptane, hexanol, and sodium dodecyl sulfate. The orientation of the nanorods was along the c-axis. TEM observations indicated that nanorods advanced in two different directions. The spacing between the horizontal and vertical lattice planes was 3.35 ± 0.01 and 3.20 ± 0.01 ångstrom, respectively. These correspond to the (110) and (001) planes of rutile SnO$_2$, respectively. The perpendicularity of the (001) plane to the nanorod axis indicates a preferential growth along the c-axis direction. Nanorods with growth direction along [1-12] were also observed.

L. Vayssieres and M. Graetzel reported the direct formation of highly ordered SnO$_2$ nanorod arrays onto various substrates (Figs. 5 and 6), which was realized in aqueous solutions at low temperatures without a template, surfactant, applied field, or undercoating. The nanorods were elongated along the c-axis and had stable prismatic (110) faces, which resulted in nanorods with a square cross section. The as-prepared nanorods were polycrystalline and consisted of bundles of finer nanorods of about 2–4 nm width (aspect ratio of about 1:100). The spacing of the lattice fringes were 0.33, 0.235, and 0.16 nm. They were indexed as (110), (111), and (002) of rutile SnO$_2$. The growth direction of the nanorods was along the c-axis.
They had side and top faces consisting of (110) and (001) planes, respectively.

Batzill et al. reported the details of the surface morphologies of SnO$_2$ (110). The excess surface free energy per unit area of (110) face was the lowest.$^{17,18}$ The (110) face was thermodynamically the most stable surface. The sequence of surface energy per crystal face was (110) < (100) < (101) < (001). Half of the surface cations are fivefold coordinated with oxygen atoms and the other half are sixfold coordinated in the (110) stoichiometric surface. The (110) face has Sn atoms with a formal oxidation state of $+\text{IV}$ because of the presence of a row of bridging oxygen atoms. Both the surface and bulk have similar resistivity. The (110) surface is a nonpolar surface because it has no net dipole moment in the [110] direction.

Beltran et al. further discussed the formation of SnO$_2$ nanoribbons that were synthesized via a carbothermal reduction process (Fig. 7).$^{18}$ They calculated the surface energy per unit area of different stoichiometric SnO$_2$ surfaces using density functional theory. In particular, the values of the free energy of formation ($\Delta G$) of each facet A on the other surface B were calculated. They concluded that the (110) surface was the most stable, which agrees with the fact that it was the predominant surface in the polycrystalline SnO$_2$ samples. Theoretical results regarding the free energy of formation and the angles between the planes and high-resolution TEM (HRTEM) observations revealed that the nanoribbons preferentially grew along the [101] crystal direction. The growth direction [101] can be represented by the (010) and (10\text{-}1) planes as surface facets with angles of 90° and 68°, respectively. The (110) plane forms facets with the (101) plane at an angle of 67°, while the other surface planes render small angles.

2.2 Development of SnO$_2$ nanostructures using cold crystallization and morphology control$^{19-22}$

The SnO$_2$ crystallization was realized in an aqueous solution of tin fluoride at 90°C following a new design of

![Fig. 3. Super-long nanobelt structure of SnO$_2$ (with rutile crystal structure). (A) SEM image of the as-synthesized SnO$_2$ nanobelts, showing a high volume percentage (>95%) of SnO$_2$ nanobelts and a small amount of Sn nanoparticles as indicated by arrows. (B to D) TEM images of SnO$_2$ nanobelts with straight and twisted shapes. An enlargement of a broken nanobelt is inserted in (B) to display the rectangle-like cross section of the belt. The belt-like shape is further verified by an enlargement of the boxed region in (C), which is displayed in (D); the width-to-thickness ratio is about 5. (E) HRTEM image of a SnO$_2$ nanobelt showing that the nanobelt is single crystalline and free from dislocation and defects. The inset shows the corresponding electron diffraction pattern recorded with an electron beam perpendicular to the long axis of a belt, showing that the growth direction is [101] (note the rutile structure of the sample). The SnO$_2$ nanobelts shown in (A), (B), and (E) were obtained by thermal evaporation of SnO$_2$ powders at 1350°C, while those presented in (C) and (D) were obtained via thermal evaporation of SnO powders at 1000°C, preserving the same crystal structure and same growth morphology.$^{13}$ Reprinted with permission from Ref. 13). Copyright 2020 The American Association for the Advancement of Science.]

![Fig. 4. a) SEM and b) TEM images of SnO$_2$ nanorods hydrothermally synthesized at 200°C for 18 h.$^{15}$ Right panel) HRTEM images of SnO$_2$ nanorods: a) survey, b, c) two individual SnO$_2$ nanorods with different growth directions.$^{15}$ Reprinted with permission from Ref. 15). Copyright 2020 John Wiley and Sons.]

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the chemical reaction in aqueous solution defined as “cold crystallization of ceramics”. In addition, morphology control of nanosheets and a structure film in which nanosheets are assembled were accomplished to develop devices for chemical sensors, etc. (Fig. 8). 19) SnO_2 nanosheets have a high specific surface area because they are only a few nanometers thick. The surface area was increased by more than 200 times that of the substrate area forming a film on a PET film or a copper foil. 20) In addition, it has a gradient structure that is suitable for chemical sensors. The surface of the assembled nanosheet film has a structure with a large opening. The inside of the assembled nanosheet film has a unique fine structure with a high surface area and additional uneven structures. Furthermore, whereas conventional SnO_2 particles have a thermodynamically stable (110) surface, the SnO_2 nanosheets prepared by this method have a metastable (101) surface. It has therefore surface characteristics that are significantly different from those of conventional SnO_2, which can be applied for various devices that utilize specific surface characteristics.

SnO_2 was produced at normal temperature, normal pressure, and in aqueous solution by this method. It is possible to form films on various materials including low-heat-resistant polymers or metals. A uniform surface film can
be generated in contact with the solution because crystal growth takes place in the solution. Therefore, uniform films can be created on a base material that is curved, has surface irregularities, is a powder, a fiber, a mesh, or is a complex structural material, etc. In addition, there are no restrictions on film formation due to the metric size. A film can also be coated on a substrate surface for a predetermined time by spraying the solution.

Careful nucleation and crystal growth of SnO\textsubscript{2} was achieved by precise control of the substrate surface. According to this method, the hydrophilic and hydrophobic regions are formed by exposing the substrate in a vacuum to ultraviolet light through a photomask. The nucleation of SnO\textsubscript{2} in the aqueous solution was promoted in the hydrophilic region and suppressed in the hydrophobic region. Patterning of the SnO\textsubscript{2} nanosheet assembled film was obtained by subsequent crystal growth into a nanosheet shape (Fig. 9).\textsuperscript{21}

A molecular sensor using a SnO\textsubscript{2} nanosheet assembled film as a semiconductor electrode was proposed. This sensor targets harmful organic molecules in rivers or industrial wastewater. The antigen–antibody reaction and photoelectric conversion were used as the sensing mechanism. Specifically, the surface of the semiconductor electrode was modified with an antibody. River water was introduced through a microchannel together with the dye-labeled antibody. The dye-labeled antibody adsorbs onto the antibody on the surface of the semiconductor electrode in the presence of the antigen. A photocurrent can be obtained by irradiating the backside of the substrate with excitation light matching the redox potential of the semiconductor and the dye. The photocurrent is proportional to the concentration of the harmful organic molecules in this system. A high surface area is required to modify the semiconductor electrodes with antibodies. Furthermore, high transparency to excitation light, high conductivity, and suppression of nonspecific adsorption are needed. Photocurrent sensing was carried out using a SnO\textsubscript{2} nanosheet assembled film on a fluorine-doped tin oxide (FTO) substrate in combination with dye Cy5.

In addition, cancer sensors for blood were developed using the SnO\textsubscript{2} nanosheet assembled film as a semiconductor electrode. This sensor targets markers of hepatocellular carcinoma. The nanosheet was modified with a dye-labeled antibody. Detection of photocurrent and fluorescence were achieved under irradiation of excitation light using SnO\textsubscript{2} nanosheets.\textsuperscript{22}

3. Development of TiO\textsubscript{2} nanostructures

3.1 Development of TiO\textsubscript{2} nanostructures and morphology control

TiO\textsubscript{2} has three distinct crystalline forms. Anatase\textsuperscript{23} and rutile\textsuperscript{24} have a tetragonal structure. Brookite has an orthorhombic structure.\textsuperscript{25} There are at least 11 phases of TiO\textsubscript{2} which include those phases.\textsuperscript{26} The columbite (α-PbO\textsubscript{2}) phase TiO\textsubscript{2}-II, a cubic fluorite TiO\textsubscript{2} phase with lattice parameter \(a = 4.516(1)\,\text{Å} \), which is observed in the
pressure range of 10–55 GPa), the baddeleyite (ZrO₂) phase, TiO₂(B), the hollandite phase TiO₂(H), the ramsdellite (MnO₂ or VO₂) phase TiO₂(R), the fluorite (CaF₂) cubic phase, TiO₂-OI (high pressure, orthorhombic OI (Pbca) structure), and the cotunnite (PbCl₂) phase TiO₂-II (cotunnite-structured OII phase; space group Pnma), the hardest oxide known, titanium is ninefold-coordinated to oxygen in the cotunnite (PbCl₂) structure. The latter phase is synthesized at pressures above 60 GPa, while temperatures above 1000 K were reported (Fig. 10). Additionally, at least three amorphous TiO₂ phases were reported: a low-density, and two high-density TiO₂ types. Swamy et al. revealed that pressure-induced amorphization (above 20 GPa) to a high-density amorphous (HDA) state occurred within anatase TiO₂ particles with sizes below \(<10\) nm. Machon et al. reported that the mechanically prepared amorphous state showed a reversible transformation from a low-density to a high-density amorphous state (HDA1) in the range of 13–16 GPa. The chemically prepared sample transformed to the high-density amorphous state (HDA2) at approximately 21 GPa. Further compression at about 30 GPa leads to the transformation of HDA2 into HDA1.

Many papers and reviews reported on TiO₂. Chemical Review, for instance, published a special issue on TiO₂ nanomaterials. Sang et al. reviewed TiO₂ nanoparticles as functional building blocks. Cargnello et al. examined the solution-phase synthesis of TiO₂ nanoparticles and nanocrystals. Wang et al. described one-dimensional TiO₂ nanomaterials: nanowires, nanorods, and nanobelts. Lee et al. evaluated one-dimensional TiO₂ nanomaterials: nanotubes. Wang and Sasaki studied TiO₂ nanosheets: graphene analogues with versatile functionalities. Fattakhova-Rohlfing et al. assessed three-

Fig. 10. Structures of 11 TiO₂ phases rendered in ball-and-stick and polyhedron models (a) rutile, (b) anatase, (c) brookite, (d) TiO₂(B), (e) hollandite-like TiO₂(H), (f) ramsdellite-like TiO₂(R), (g) cotunnite-like TiO₂(II), (h) baddeleyite-like phase, (i) OI phase, (j) cotunnite-like OII phase, and (k) fluorite-like cubic phase. Red balls: O atoms; blue balls: Ti atoms. Unit cells are outlined using thin lines. Reprinted with permission from Ref. 26). Copyright 2020 American Chemical Society.
dimensional TiO₂ nanomaterials.⁴³) Liu et al. commented on TiO₂ crystals with tailored facets.⁴⁴) Zhang et al. examined the structural characteristics, and mechanical and thermodynamic properties of nanocrystalline TiO₂.²⁶) Coppens et al. determined the crystallography and properties of polyoxometalate nanoclusters.⁴⁵) Kapilashrami et al. studied the optical properties and electronic structure of TiO₂ nanomaterials for renewable energy applications.⁴⁶) Angelis et al. reported theoretical studies on anatase and less common TiO₂ phases: bulk, surfaces, and nanomaterials.⁴⁷) Bourikas et al. discussed TiO₂ (anatase and rutile): surface chemistry, liquid-solid interface chemistry, and scientific synthesis of supported catalysts.⁴⁸) Asahi et al. evaluated nitrogen-doped TiO₂ as a visible-light-sensitive photocatalyst: designs, developments, and prospects.⁴⁹) Dahl et al. studied composite TiO₂ nanomaterials: self-structured modifications.⁵¹) Schneider et al. highlighted the understanding of TiO₂ photocatalysis: mechanisms and materials.⁵²) Ma et al. reviewed TiO₂-based nanomaterials for photovoltaic fuel generation.⁵³) Liu et al. assessed bio-inspired TiO₂ materials with special wetting ability and their applications.⁵⁴) Bai et al. investigated TiO₂ nanomaterials for photovoltaic applications.⁵⁵) Bai et al. examined TiO₂ nanomaterials for sensor applications⁵⁶) and Rajh et al. commented on TiO₂ in the biomedical revolution.⁵⁷)

Gordon et al. studied TiO₂ particles including tetragonal bipyramidal anatase and anatase nanoplates.⁵⁸) They were synthesized using seeded growth.⁵⁹)–⁶¹) All syntheses were performed using the standard Schlenk line technique under nitrogen atmosphere. The introduction of titanium(IV) fluoride (TiF₄) preferentially exposed the {001} facet of anatase through in situ release of hydrofluoric acid (HF), forming uniform anatase based on the truncated tetragonal bipyramidal geometry. A method was described to engineer the percentage of {001} and {101} facets choosing specific cosurfactants and titanium precursors. TiF₄ produced highly uniform tetragonal bipyramidal anatase nanocrystals (sample F-oleylamine), which were significantly truncated perpendicular to the [001] direction [Fig. 11(a)] in the presence of the cosurfactant oleylamine. TiCl₄ generated pure phase brookite nanorods (Cl-oleylamine) similar to those reported previously⁵⁹) [Fig. 11(c)]. The cosurfactant 1-octadecanol provided anatase nanoplates (F-octadecanol) with a high percentage of {001} facets [Fig. 11(d)] in the TiF₄ system. Using TiCl₄ resulted in tetragonal bipyramidal anatase nanocrystals (Cl-octadecanol) with primarily {101} facets [Fig. 11(f)]. Fluorine-containing species caused the preferential exposure of the {001} facet of anatase, and truncated the bipyramidal base morphology of the nanocrystals.⁵²,⁶³) In addition, oxygen vacancies were formed in the presence of fluorine (TiF₄) to color TiO₂ blue. The photocatalytic activity of platinized TiO₂ nanocrystals was also tested with respect to hydrogen evolution in the presence of methanol as a sacrificial model agent. TiO₂ nanocrystals with more {101} facets showed the highest activity, which is consistent with recent experimental reports.

The structure of an approximately 5 nm anatase particle in vacuum was predicted using molecular dynamics (MD) simulations.²⁶) The particle had an interior bulk crystalline structure of anatase and a thin amorphous surface layer. The surface structures that were characterized having many dangling bonds are significantly distorted (relative to the bulk counterparts) as a result of the energy minimization of the whole particle as one system.

Barnard et al. calculated structures, surface energies, and surface tensions, and discussed the effects of particle morphology and surface hydrogenation on the phase stability of TiO₂.⁶⁴) They used density functional calculations to accurately determine surface energies and surface tensions. Hydrogenated surfaces were calculated to discuss protonated TiO₂ surfaces in highly acidic aqueous conditions. Anatase (001), (100), (110), and (101) and rutile (001), (100), (110), and (011) were considered (Fig. 12). Typical Wulff-constructed morphologies of ana-

![Fig. 11. TEM images of TiO₂ nanocrystals synthesized using (a, d) the precursor TiF₄, (b, e) a mixed precursor of TiF₄ and TiCl₄, and (c, f) TiCl₄. The nanocrystals depicted were synthesized in the presence of (a-c) oleylamine and (d-f) 1-octadecanol, respectively.⁵⁶) Reprinted with permission from Ref. 58). Copyright 2020 American Chemical Society.]
tase and rutile were calculated (Fig. 13). It was identified that the surface energies of rutile are higher than those of anatase over a wide range, consistent with previous calculations.\(^6\)\(^5\)\(^6\)\(^7\) The free energy for anatase and rutile crystals was calculated as a function of the number of TiO\(_2\) units. The crossover average sizes were 9.3 nm for anatase and 9.0 nm for rutile with clean surfaces. Anatase had a lower free energy than that related to the 9.3 nm particle size. The sizes of partially hydrogenated surfaces are 8.9 nm for anatase and 8.6 for rutile. In contrast, fully hydrogenated surfaces showed larger sizes, 23.1 nm for anatase and 22.1 nm for rutile. The calculation of spherical particles indicated (not Wulff shapes) a crossover size of about 2.6 nm. This was close to those obtained by MD\(^6\)\(^8\)\(^9\)\(^\)\(^1\)\(^0\)\(^5\)\(^\)\(^6\)\(^7\)\(^8\)\(^9\) and other density functional theory (DFT) calculations.\(^\)\(^1\)\(^1\)\(^3\).

Zhou et al. reported first-principles calculations based on DFT (Fig. 14).\(^6\)\(^9\) These indicated that the Wulff shape of an anatase nanocrystal was a truncated bipyramid exposing low-energy \{101\} and \{001\} surfaces, whereas the Wulff construction for rutile exhibits \{110\} and \{101\} facets.\(^6\)\(^6\)\(^7\)\(^0\)\(^7\)\(^1\) Zhou et al. reported that phase stability reversal occurs at approximately 267 TiO\(_2\) units for the energy-minimized shapes of anatase and rutile.\(^6\)\(^9\) Wulff-shaped anatase particles were stable at 267 TiO\(_2\) units or less, which corresponds to an anatase particle that is 2.1 nm thick along the normal (101) plane and 3.6 nm long in the [001] direction.

Anatase and rutile phases are widely used in electronic devices, optical devices, and biomaterials, etc. Various nanostructures were synthesized to improve their properties. Liu et al. reported the equilibrium crystal shape of anatase TiO\(_2\) (Fig. 15) and rutile TiO\(_2\) (Fig. 16) determined by Wulff construction and evolved other shapes.\(^4\)\(^4\)

Amano et al. synthesized octahedral anatase crystals with a c-axis lengths of <100 nm and exposed anatase \{101\} facets (Fig. 17).\(^7\)\(^2\) These were prepared by hydrothermal treatment of K-titanate nanowires (the molar ratio of K to Ti is ca. 12%) in Milli-Q water at 170°C. Anatase crystallizes with abundant \{101\} facets effectively decomposed organic compounds by photocatalytic oxidation in the presence of molecular oxygen. In contrast, the anatase (101) surface was not as effective as other surfaces exposed to ordinary anatase particles to generate H\(_2\) in the absence of molecular oxygen.

Wu et al. synthesized single-crystalline anatase TiO\(_2\) nanobelts with two dominant surfaces of \{101\} facets by calcining protonated titanate (nanofibers) at 700°C for 30 min using a ramp rate of 1 °C/min (Fig. 18).\(^7\)\(^3\) The \{101\} facets exhibited an enhanced photocatalytic activity compared to their nanosphere counterparts with identical crystal phases and similar specific surface areas. The ab initio DFT calculations show that the exposed \{101\} facet of the nanobelts yields an enhanced reactivity with molecular O\(_2\), facilitating the generation of superoxide radicals. Moreover, the nanobelts provide a lower electron–hole recombination rate than the nanospheres because of the following three reasons: (i) greater charge mobility in the
nanobelts, which is enabled along the longitudinal dimension of the crystals; (ii) fewer localized states near the band edges and in the bandgap due to fewer unpassivated surface states in the nanobelts; and (iii) enhanced charge separation due to trapping of photogenerated electrons by chemisorbed molecular O$_2$ on the $\{101\}$ facet.

Anatase crystals with $\{001\}$ facets are rare because of their high surface energy of 0.90 J m$^{-2}$. Theoretical predictions about the ($001$) surface suggested promising properties such as the dissociative adsorption of water molecules (69) and the unique anchoring of dye molecules. (70) Yang et al. synthesized micrometer-sized anatase single crystals with a large percentage of $\{001\}$ facets by a hydrothermal method using TiF$_4$ and HF as the Ti precursor and morphology-controlling agent, respectively. (62) The resultant crystals appeared as highly truncated bipyramids with two square ($001$) surfaces and eight isosceles trapezoidal ($101$) surfaces.

Menzel et al. reported anatase nanoplatelets with $\{001\}$ facets (Fig. 19) and a ternary diagram (Fig. 20). (74) The diagram illustrates the dependence of the TiO$_2$ nanoparticle morphology on the molar ratio of titanium source, fluoride source, and water. Two-dimensional TiO$_2$ anatase nanoplatelets were synthesized via the solvothermal reaction of titanium(IV) isopropoxide in the presence of structure-directing hydrogen fluoride. Nanoplatelets are heavily truncated octahedral TiO$_2$ anatase nanocrystals with a large fraction of high-energy $\{001\}$ crystal facets. Depending on the composition of the reaction system, oriented attachment of the anatase nanoplatelets along either the $\{001\}$ or $\{101\}$ facets is observed. The photocatalytic activity of nanocrystals with different aspect ratios, determined in dye degradation experiments, demonstrated a higher activity of the $\{001\}$ compared to the $\{101\}$ anatase facets.

Li et al. reported the synthesis of tetragonal faceted-nanorods of anatase TiO$_2$ single crystals with a large per-

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**Fig. 14.** Potential energy of (a) series of (quasi-)Wulff shapes of anatase (A, red symbols) and rutile (R, green symbols) with various length-to-width ratios; (b) minimum-energy shapes as a function of the number of TiO$_2$ units. The size of the particle (in nanometers) along the normal ($101$) plane for anatase and $[110]$ direction for rutile is given in parentheses. O ions are red and Ti ions are gray. (69) Reprinted with permission from Ref. 69). Copyright 2020 American Chemical Society.

**Fig. 15.** Equilibrium crystal shape of anatase TiO$_2$ determined by Wulff construction and evolved other shapes. (44) Reprinted with permission from Ref. 44). Copyright 2020 American Chemical Society.

**Fig. 16.** Left panel: Equilibrium crystal shape of rutile TiO$_2$ using Wulff construction (264) and (right panel) the evolved other shapes of rutile TiO$_2$. (44) Reprinted with permission from Ref. 44). Copyright 2020 American Chemical Society.

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The percentage of active \{100\} facets (Fig. 21). This process involves the formation of Na-titanate nanotubes by the hydrothermal reaction of P25 in a NaOH solution and the subsequent hydrothermal transformation of the precursors into the anatase phase of TiO$_2$ in a basic solution. The nanorods with \{100\} facets exhibited much higher
photocatalytic activities (2.2 times) than those of commercial anatase powders having normal majority \{101\} facets because of the large percentage of \{100\} facets.

Zhao et al. reported anatase TiO\(_2\) nanocuboids enclosed by active \{100\} and \{001\} facets (Fig. 22).\(^{77}\) They were solvothermally synthesized through hydrolysis of titanium tetraisopropoxide (TTIP) using acetic acid (HAc) as the solvent and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF\(_4\)]) as the capping agent.

3.2 Development of TiO\(_2\) nanostructures using cold crystallization and morphology control\(^{78}\)–\(^{86}\)

The synthesis of TiO\(_2\) with an aqueous solution process was reviewed in a paper by Prof. Mark R. De Guire.\(^{78}\)
After developing an amorphous TiO$_2$ film (method 1 in ref. 78), crystallization of TiO$_2$ in an aqueous solution was realized by precise control of temperature, pH, etc. [Method 2 in reference (78)].

Synthesis of an acicular TiO$_2$ crystal-oriented film and analysis of its microstructure were carried out by further developing these methods. The acicular crystals were anatase-type TiO$_2$ grown anisotropically in the c-axis direction. They grew vertically on the substrate, forming an acicular TiO$_2$ crystal-oriented film with a high c-axis orientation (Fig. 23). These materials are promising as a sensor that requires an uneven surface structure or as a surface modification layer for various substrates. Another feature that is different from conventional TiO$_2$ is its fine structure.

X-ray diffraction (XRD) showed a high c-axis orientation. TEM observations showed that the c-axis of anatase-type TiO$_2$ was oriented in the longitudinal direction of the needle-shaped crystals. In contrast, a fine structure different from the single crystal was observed in high-resolution TEM images. It was a connected structure in which minute single crystal regions of approximately several nm are linked. They uniformly oriented the c-axis in the longitudinal direction of the needle-shaped crystal. Moreover, the contrast of lattice fringes in the high-resolution observation was weak and unclear compared with that of the single-crystal TiO$_2$. This crystalline TiO$_2$ was expected to contain many defects. It is a novel material with a characteristic microstructure which is different from conventional TiO$_2$ crystals.

Acicular TiO$_2$ crystal-assembled particles were synthesized with this method. They had a BET specific surface area of 270 m$^2$ g$^{-1}$, higher than that of commercial nanoparticles AEROXIDE TiO$_2$ P25 (BET specific surface area: 50 m$^2$ g$^{-1}$, particle size: 21 nm). They were porous particles composed of needle-like crystals that grew anisotropically in the c-axis direction.

Large multi-needle particles were also synthesized using this method. Acicular crystals grew radially from the center of the particles. The longitudinal direction of each acicular crystal was the c-axis direction of anatase-type TiO$_2$, which indicated anisotropic crystal growth in the c-axis direction. In addition, a characteristic unclear contrast showing defects and low crystallinity was observed with high-resolution observation (Fig. 24).

Furthermore, the surface of the acicular TiO$_2$ crystal-oriented film was modified with dye-labeled DNA for liquid phase molecular sensors. The sensor successfully achieved fluorescence detection under excitation light. The fluorescence intensity was approximately three times higher than that of the TiO$_2$ film prepared with the nanoparticles AEROXIDE TiO$_2$ P25. It was also observed that heat treatment at 500 °C reduced the fluorescence intensity by half. These sensors displayed a characteristic surface structure, internal structure, defects, crystallinity, orientation, and a fine single crystal-connected structure.
4. Development of ZnO nanostructures

4.1 Development of ZnO nanostructures and morphology control

ZnO is wurtzite-structured and crystallizes in the hexagonal P6\textsubscript{3}mc space group. Various ZnO nanomaterials are reported to control crystal growth. ZnO nanomaterials are based on the hexagonal symmetry. 1D nanomaterials such as nanorods or wires can be synthesized with anisotropic crystal growth along the \textit{c}-axis. Two dimensions (2D) nanodisks or nanoplates can be prepared with crystal growth along the \textit{a}-axis. The control of crystal growth conditions or capping materials was widely used to manipulate the morphology. A. Umar and Y. B. Hahn edited a five volume book set about ZnO nanostructures.\textsuperscript{87} They focused on growth, properties, applications, ZnO nanostructures, and nanodevices. Many reviews and papers also reported on ZnO nanostructures due to their valuable applications. Ü. Özgür et al. issued a comprehensive review of ZnO materials and devices.\textsuperscript{88} Wang et al. described ZnO nanostructures, defects, and devices.\textsuperscript{89} Jun evaluated the shape control of semiconductor and metal oxide nanocrystals through nonhydrolytic colloidal routes.\textsuperscript{90} Agnieszka et al. reviewed ZnO from synthesis to application.\textsuperscript{91} Fan et al. studied the ZnO nanostructures, synthesis, and properties.\textsuperscript{92} These articles documented valuable research on ZnO nanostructures.

Li et al. synthesized hexagonal disks and hexagonal rings using a sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT) microemulsion. A solution containing Zn(NO\textsubscript{3})\textsubscript{2}·6 H\textsubscript{2}O (0.025 M), NaAOT (0.10 M), NH\textsubscript{3}·H\textsubscript{2}O (17.65 M), water, and 1-butanol was maintained at either 70 or 90 °C for 5 days (Fig. 25).\textsuperscript{93} The disks were 2–3 \textmu m in diameter and 50–200 nm thick. Some of the disks had a hole in the middle and were thus hexagonal rings. The disk had a single-crystal structure, with (0001) top/bottom surfaces and \{1-100\} side facets. Fast growth along \{2-1-10\} result-
ed in the formation of a hexagonal disk. The top and bottom surfaces of the hexagonal rings and disks were quite different. One side was a smooth surface, while the other one was rough with a higher “etching” rate. The disk had defects, which were distributed radially with a higher concentration at the center. The defects were most likely low-angle grain boundaries. Excess NH₃·H₂O etched a negatively charged O²⁻ (000-1) surface. A higher etching/reaction rate was possible at the defect sites. Therefore, a high density of planar defects at the center resulted in a higher local etching rate and eventually led to the formation of a hole at the center. A rough edge at the inner surface was apparent for a small hole.

Han et al. reported ZnO flakes, columns, and pyramids provided by different facile wet chemical routes (Fig. 26).⁹⁶) ZnO flakes were prepared either by the technique reported by Jang et al.⁹⁷) or via a hydrothermal route described below. The flakes were prepared in a hydrothermal solution containing 0.287 g of ZnSO₄·4H₂O, 0.080 g of NaOH, 0.083 g of NaF, 7 mL of distilled water, and 3 mL of ethanol at 200 °C for 24 h. ZnO columns were synthesized in a hydrothermal solution containing 0.66 g Zn(CO₂CH₃)₂·2H₂O, 2.4 g NaOH, 21 mL of glycerin, and 9 mL of distilled water at 150 °C for 24 h. ZnO pyramids were generated by the thermal decomposition of Zn(CO₂CH₃)₂ in a mixed solvent of organic amine and carboxylic acid.⁹⁸) In a typical experiment, 1.46 g anhydrous zinc acetate [Zn(CO₂CH₃)₂] was added to a mixed solvent of 6.6 mL of oleic acid and 4.5 mL of ethylenediamine. The resulting mixture was heated at 286 °C for 10–15 min. The order of gas sensing and photocatalytic efficiency of the ZnO crystal planes was (0001) > {10-10} > {10-11} and (000-1).

Park et al. fabricated wide ZnO nanosheets on an Au-coated silicon substrate by heating a 1:1 mixture of ZnO and graphite under a constant flow of gases for 5–120 min at 800–950 °C (Fig. 27).³⁹) The amount of additional oxygen was controlled in the range of 1–20% with 20 cm³ min⁻¹ of Ar. The thickness of the Au coating was 5–30 Å. First, 1D nanowires grew. Thereafter, dendritic side branch nanowires began to grow along the basal nanowires, resulting in highly defined and aligned comb-like architectures. The side branches continued to grow, and planar filling of the interspaces between the evenly spaced side branches proceeded, eventually resulting in an ultrawide nanosheet. The width and thickness of the sheets were in the ranges of 50–100 μm and 50–100 nm, respectively. The width-to-thickness ratios of the sheets reached up to one thousand.

Xingfu et al. reported the microspherical organization of multilayered ZnO nanosheets (Fig. 28).¹⁰⁰) A solution containing 0.002 mol of Zn(NO₃)₂·6H₂O, 0.01 mol of urea, cetyltrimethlammonium bromide (CTAB), 5–10 mL of 1-butanol, and 50 mL of deionized water was heated to...
100–150 °C for 8–24 h. The hydrothermal product was a typical metal hydroxide salt, Zn₄(CO₃)(OH)₆·H₂O, having lamellar structure. It was converted to a ZnO multilayered structure by annealing at 300 °C for 5 h. Flower-like microspheres were generated using ZnO nanosheets. The diameter of the microspherical assembly was approximately 15 μm. The building blocks, ZnO nanosheets with a length of about 7 μm and a thickness of several nanometers, were precisely aligned from the microspherical assembly in a dispersive mode.

Huang et al. synthesized ZnO polycrystalline nanosheets on Cu substrates by deposition using a chemical bath followed by heat treatment. Cu foil was kept in solution containing 150 mL of 0.05 M Zn(NO₃)₂, 150 mL of 1 M CO(NH₂)₂, and 150 mL of deionized water at 80 °C for 1 h. The nanosheets were annealed under flowing argon at 350 °C for 45 min and showed initial discharge and charge capacities of 1120 and 750 mAh g⁻¹ when cycled at 0.05 A g⁻¹. Stable capacities of 400 mAh g⁻¹ for up to 100 cycles at 0.5 A g⁻¹ were maintained. Cheng et al. reported oriented ZnO nanoplates on an Al substrate. The Al substrate was immersed in a solution containing an equal volume of a zinc nitrate [Zn(NO₃)₂] solution with concentrations varying from 0.02 to 0.2 M and a hexamethylenetetramine (HMT) solution (0.02 to 0.2 M) for 2 h at 90–150 °C. They were then annealed at 500 °C for 1 h. The top and bottom surfaces of the nanoplates were ZnO (001) facets. However, these ZnO nanoplates are easily converted into polycrystalline ZnO under electron beam irradiation, proving that these ZnO nanoplates are metastable.

Pan et al. synthesized ZnO nanobelts by the thermal evaporation of ZnO powders at 1400 °C for 2 h (Fig. 29). They had a rectangle-like cross section. The thickness and width-to-thickness ratios of the nanobelts were in the ranges of 10 to 30 nm and 5 to 10, respectively. The nanobelts were single crystalline, but with two different growth directions. The nanobelt growing along [0001] and enclosed by (2-1-10) and (01-10) facets shows no defect and no dislocation; the one growing along [011-0] and enclosed by (0001) and (2-1-10) facets is also dislocation-free, displaying only a single stacking fault that is parallel to the axis and runs through the entire length of the nanobelt. No particles were observed at the ends of the nanobelts. The ripple-like contrast observed in the TEM image is due to the strain resulting from the bending of the belt.

Kong et al. reported the synthesis of ZnO nanorings via a spontaneous self-coiling process during the growth of polar nanobelts (Fig. 30). They had a rectangle-like cross section. The thickness and width-to-thickness ratios of the nanobelts were in the ranges of 10 to 30 nm and 5 to 10, respectively. The nanobelts were single crystalline, but with two different growth directions. The nanobelt growing along [0001] and enclosed by (2-1-10) and (01-10) facets shows no defect and no dislocation; the one growing along [011-0] and enclosed by (0001) and (2-1-10) facets is also dislocation-free, displaying only a single stacking fault that is parallel to the axis and runs through the entire length of the nanobelt. No particles were observed at the ends of the nanobelts. The ripple-like contrast observed in the TEM image is due to the strain resulting from the bending of the belt.
ZnO crystal had several alternating planes composed of tetrahedral coordinated O$_2^-$ and Zn$_2^+$ ions, stacked alternately along the c-axis. Positively charged (0001)-Zn and negatively charged (0001)-O polar surfaces were observed. The polar nanobelt grew along [10-10], with side surfaces (1-210) and top/bottom surfaces (0001) and had a typical width of about 15 nm and a thickness of around 10 nm. The positively charged (0001)-Zn plane was attached to the negatively charged (0001)-O plane (bottom surface) to reduce the electrostatic energy. This resulted in the neutralization of the local polar charges and in a reduced surface area, thus forming a loop with an overlapped end.

The whisker shape is one of the typical morphologies of ZnO. Hu et al. realized micropatterning of ZnO nanowhiskers on a self-assembled monolayer (Fig. 31). Doped SnO$_2$-coated glass substrates were immersed in a solution containing a 200 mL aqueous solution of 0.1 M zinc nitrate, 0.1 M hexamethylenetetramine, and 0.02 M polyethylenimine at 88 °C for 30 min. ZnO whiskers were grown on the hydrophilic regions of the substrate. They were generated perpendicular to the substrate and grew along the c-axis to form a 1D whisker shape. The whisker shape is one of the typical morphologies of ZnO. Hu et al. realized micropatterning of ZnO nanowhiskers on a self-assembled monolayer (Fig. 31). Doped SnO$_2$-coated glass substrates were immersed in a solution containing a 200 mL aqueous solution of 0.1 M zinc nitrate, 0.1 M hexamethylenetetramine, and 0.02 M polyethylenimine at 88 °C for 30 min. ZnO whiskers were grown on the hydrophilic regions of the substrate. 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the crystal growth (zinc oxide: hexagonal wurzite type). In particular, the formation of a ZnO nanosheet-assembled gradient-oriented film showed a high potential for crystal growth and morphology control in aqueous solution processes (Fig. 32). The liquid surface of the zinc ion-containing aqueous solution was used as the reaction field in this method. ZnO crystal nuclei were generated at the air-liquid interface by precise control of the chemical reaction near the liquid surface. The crystals were then grown in a specific direction into the liquid (downward direction). The anisotropic growth was realized by supplying source ions only from the solution direction. The crystal morphology was then manipulated into a nanosheet shape by controlling the solution condition. The ZnO nanosheet was grown in the a-axis direction and had large c-crystal faces. In contrast, structures based on ZnO hexagonal columns were formed in the solution by anisotropic growth in the c-axis direction excluding the air-liquid interface. This showed that morphology control of nanosheets with large c-crystal faces was provided by precisely managing the local solution conditions near the air-liquid interface. In addition, several factors were considered to fabricate the gradient structure. The reaction conditions were changed with time by continuously adjusting the solution conditions, such as the decrease in ion concentration. This was effective to continuously alter the nanosheet size, etc. The gradient film was accomplished consistently modifying the size, density, and orientation of the nanosheets in the direction perpendicular to the film. This was a pioneering study of creating novel microstructures by incorporating multiple new concepts regarding crystal growth control, which indicated the high potential for cold crystallization and morphology control. It serves as a valuable guideline for the nano-structuring of ceramics.

The morphology of ZnO can be manipulated to obtain a dense film as well as an integrated film of hexagonal
column crystals or a whisker film with a sharp tip because of the hexagonal crystal structure. Seed layer formation using a high temperature treatment was indispensable for many years in the synthesis of ZnO films from aqueous solutions. The direct-oriented growth of ZnO crystals on a substrate was realized without a seed layer. The direct formation of ZnO crystals was achieved on SnO2 crystal surfaces of FTO, as seen in TEM images (Fig. 33). A micropatterning technique for ZnO whisker films was also developed using seed layer formation by patterned exposure through a photomask.

Furthermore, a liquid-phase molecular sensor was developed using a c-axis-oriented ZnO rod array on a FTO substrate as a semiconductor electrode. Surface modification of ZnO with dye-labeled DNA was used for the sensor. A photocurrent was detected under excitation light. High signal-to-noise ratios of over 50 were achieved with this ZnO rod array-type sensor. This technique can be applied to generate similar liquid-phase molecular sensors.

5. Conclusions

“Cold crystallization” is studied since the introduction of ceramics. Energy savings, low environmental impact, and hybridization with other materials could be achieved by better understanding this phenomenon. These are major issues that need to be investigated in the field of ceramics. Furthermore, “morphology control” is one of the main challenges that has to be addressed to develop new functions for future applications. In particular, applications such as sensors, batteries, biomaterials, catalysts, surface treatments, and composite material interfaces, whose properties are considerably affected by the microstructure of the surface and the inside of the materials, are of importance.

The studies reviewed in this paper laid the foundation for “cold crystallization” and “morphology control”; however, to understand the fundamentals and to harvest the benefits of these processes needs the participation of further researchers and engineers.

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