

## Designing ordered nanoarrays from aqueous solutions\*

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*Abstract:* The design and large-scale fabrication of ordered arrays consisting of advanced and well-defined building blocks such as quantum dots, nanorods, and nanowires is essential to the creation of new devices based on nanoscience. A concept as well as a growth model and a thin film technique have been developed by the author to contribute to these challenges. These ideas and synthesis method led to the creation of a new generation of functional materials from aqueous solutions with designed morphology and orientation, which are in better adequacy with their applications. Nanomaterials are growing directly onto various substrates by heteronucleation from the thermohydrolysis of aqueous metal salt precursors. Although this bottom-up technique allows the generation of anisotropic and oriented building blocks of various length scales and on many types of substrates, it is carried out without template, surfactant, applied field, or undercoating. Therefore, high-purity, low-cost, and large-scale fabrication of advanced nanomaterials is achieved. In addition, the direct contact growth between 1-D building blocks and their substrate is an essential feature to take full advantage of oriented nanorods, that is, a direct path for electron/hole transport. This specific conformation is of particular interest in developing more efficient devices such as sensors and photovoltaic cells.

*Keywords:* nanostructures; metal oxide; low dimensionality; materials chemistry; interfacial thermodynamics.

### INTRODUCTION

A plethora of exciting novel and more complex nanostructures [1] have emerged in the recent years besides carbon nanotubes [2] and metal nanoparticles [3]. Such novel and ordered 0- [4] and 1-D [5] building blocks [6], 2-, and 3-D nanostructures are produced to fabricate future functional nanodevices such as nanolasers and optoelectronic devices [7], nanotransistors [8], nanosuperconductors [9], nanophotonics [10], nanocomputers [11], nanosensors [12], and nanofilters [13] as well as applications in biotechnology [14] and medicine [15]. In addition to applied research, fundamental studies of their electronic structure [16], structural [17], magnetic [18], optical [19], chemical [20], and mechanical [21] properties have been pursued to reach better fundamental knowledge of nanosystems. Novel and ingenious lithographic [22] and non-lithographic [23] patterning techniques including proton beam writing [24] have also been developed with good accuracy and reproducibility down to a few hundred nanometers to exploit the tremendous potentials of ordered nanomaterials for high-tech and future applications [25] as well as more conventional ones [26]. In almost all applications, fabrication represents one of the most important challenges to their realization and commercialization. Indeed, besides very few exceptions, the production needs of cheap, clean, reliable, and durable materials with controlled

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properties for realistic and practical applications of nanotechnology, and the request of mass production of thin film devices still represent one of the most important issues of the development of future devices. Materials chemistry [27] has emerged as the most consistent fabrication tool to deliver high-purity functional nanomaterials at low cost and large scale engineered from molecular to microscopic scale. A review of the major achievements and recent advances of a recently developed low-temperature aqueous chemical growth technique for the fabrication of purpose-built metal oxide nanomaterials [28] and ordered arrays from solutions are exposed hereafter.

## THEORETICAL CONSIDERATIONS

Ultra-divided systems such as nanoparticle dispersions are generally unstable with regard to the size and number of their constituents because the solid-solution interfacial tension, acting as a driving force, leads to a spontaneous reduction of the surface area to minimize the dispersion free enthalpy. Such a phenomenon, known as surface energy minimization, induces an increase in average particle size as a result of the reduction of the surface area at constant volume. For such a reason, such dispersions are usually considered thermodynamically unstable. However, they can be thermodynamically stabilized if, by adsorption, the interfacial tension of the system becomes very low. This phenomenon, well known for microemulsions [29], was for the first time quantitatively modeled and demonstrated for transition-metal oxide nanoparticles [30]. When the pH and the ionic strength of the aqueous precipitation/dispersion medium are sufficiently high, the ripening of nanoparticles is avoided and their size can be monitored over an order of magnitude by tailoring solution pH and ionic strength. A model based on Gibbs adsorption equation [31] led to an analytical expression of the water-oxide interfacial tension as a function of the pH and the ionic strength of the dispersion/precipitation medium. The stability condition, defined by a “zero” interfacial tension, corresponds to the chemical and electrostatic saturation of the water-oxide interface. In such a condition, the density of charged surface groups reaches its maximum and further adsorption forces the surface area to expand and, consequently, the size of nanoparticles to decrease. The model did account very well for the experimental results obtained from the aqueous precipitation of magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles in basic medium [32]. The excellent agreement between theoretical modeling and experiments led strong evidence for a general efficient growth control of metal oxide nanoparticles under low interfacial tension conditions.

An essential next step has been to follow the same concept to develop the capability of growing nano- to microparticulate thin films from aqueous solutions and controlling the orientation of large arrays of anisotropic nanoparticles onto a substrate [33]. To achieve such a challenge, one has to consider the differences between homogeneous and heterogeneous nucleation phenomena. In most cases, homogeneous nucleation of solid phases from solutions requires a higher activation energy barrier, and, therefore, heteronucleation is promoted and energetically more favorable. Indeed, the interfacial energy between two solids is generally smaller than the interfacial energy between a solid and a solution, and, therefore, nucleation may take place at a lower saturation ratio onto a substrate than in solution. Nuclei will grow by heteronucleation onto the substrate, and various morphologies and orientation monitoring can be obtained by experimental control of the chemical composition of the precipitation medium.

In addition to the control of particle size, shape, and orientation, heteronucleation at low interfacial tension allows the stabilization of oxide and oxyhydroxide metastable crystal structures. Crystal-phase transitions in solution generally operate through a dissolution–recrystallization process to comply with the surface energy minimization requirement of the system. Indeed, when a solid offers several allotropic phases and polymorphs, it is typically the one with the highest solubility and consequently the lowest stability (i.e., the crystallographic metastable phase), which precipitates first. This is understood by considering the nucleation kinetics of the solids. At a given supersaturation ratio, the germ size is as small (and the nucleation rate as high) as the interfacial tension of the system is low. Thus, given that the solubility is inversely proportional to the interfacial tension, the precipitation of the most soluble phase and consequently the less stable thermodynamically, is therefore kinetically promoted. Due

to its solubility and metastability, this particular phase is more sensitive to secondary growth and aging, which leads to more stable phases, essentially by heteronucleation. Secondary growth and aging processes are delicate to control, and the phase transformations appear within a few hours to a few days in solution, whence the resulting undesired mixing of allotropic phases and polymorphs. However, by careful consideration of the precipitation conditions (i.e., at thermodynamically stable conditions), such phenomena may be avoided when nanosystems are precipitated at low interfacial tension [34].

In summary, by adjusting the experimental conditions to reach the thermodynamic stability of a system, the nanoparticle size, shape, and crystal structure may be tuned and optimized. It allows the functionalized design of ordered nanoarrays and thus the ability to quantitatively probe the influence of such parameters on the physical and chemical properties of metal oxide nanoparticles and nanoparticulate materials. Although such bottom-up techniques allow the generation of anisotropic and oriented building blocks of various length scales and on various types of substrates (polycrystalline, single-crystalline, or amorphous), it is carried out without template, surfactant, applied field, or undercoating. Therefore, high-purity, low-cost, and large-scale fabrication of advanced nanomaterials is achievable. In addition, a direct growth (contact) between 1-D building blocks and their substrate is essential to take full advantage of oriented nanorods, that is, a direct path (free of grain boundaries) for electrons, for instance. Such a conformation is of particular interest for developing more efficient devices, for example, gas sensors, photovoltaic cells, and photocatalysts.

## ACHIEVEMENTS

The first successful achievement of this concept has been the development of thin films of hematite consisting of oriented nanorods [35]. Such a design was conceived to demonstrate that hematite was indeed capable of withdrawing photogenerated electrons in a 2-electrode (sandwich-type) wet photovoltaic cell. Over the last decades, many attempts to make use of hematite as a solar cell in view of its very attractive characteristics such as, for instance, a 2 eV bandgap, low cost, and nontoxicity, have been pursued. However, the main conclusion has been that bulk or surface recombinations were too high for any practical applications [36]. The fabrication of porous nanostructured hematite thin film consisting of nanoparticles of 10–15 nm in diameter also showed very low efficiency even under polychromatic light [37] due to high recombination losses.

We developed anisotropic crystallites of hematite elongated along the *c*-axis, e.g., where the dielectric constant is the highest and where the diameter of such nanorods is matching the minority carrier (hole) diffusion length (reported to be around 2 to 4 nm [38]). Thus, enhanced charge separation and photoconversion efficiency were predicted and demonstrated. Indeed, the fabrication of porous photoanodes consisting of large arrays of perpendicularly oriented single-crystalline hematite nanorods of 4 nm in diameter and 500 nm in length, aggregated in 50 nm in diameter bundles, grown on transparent conductive oxide (TCO) such as fluorine-doped tin oxide glass, allowed efficient charge separation by fast hole release from the valence band and fast capture at the electrode/electrolyte interface by a redox couple. Therefore, such a designed pathway for photogenerated electrons overcomes most of the electron-scattering and recombination processes at grain boundaries and substantially lowered the well-known hematite bulk recombination losses. As predicted, a better collection of photogenerated electron was achieved, improving the photoconversion efficiency, and yielded to a relatively good photovoltaic response and thus, the development of the first iron oxide wet photovoltaic cells [39].

Moreover, 1-D electron quantum confinement effect in such ultrafine nanorods has been suggested to contribute to the unusually high efficiency of these photovoltaic nanodevices. The investigation was carried out at a synchrotron radiation facility by soft X-ray resonant inelastic scattering (RIXS) and absorption techniques [40]. The results clearly indicate a significant increase of the bandgap of hematite ultrafine nanorods compared to more conventional polycrystalline or single-crystalline samples ca. 1.9–2.1 to 2.5 eV. Besides the fundamental understanding of low dimensionality and quantum

confinement effect on the electronic structure of large bandgap semiconductor, this result opens up the possibility of generating hydrogen with an iron oxide anode and such, without applied bias.

Following the same idea for the design of functional large bandgap semiconductor [41] nanostructures for photovoltaics and photocatalytic devices [42], we have been developing large arrays of perpendicularly oriented and fairly well-aligned zinc oxide hexagonal microrod- [43] and nanorod- [44] arrays. A good control over diameter (from 10 nm to 1  $\mu\text{m}$ ) and rod length (from 0.1 to 10  $\mu\text{m}$ ) was obtained. The electron transport of such material was found to be very efficient, with very low level of dark current, and almost no losses at the electrolyte/electrode interface were found under UV illumination. These rods are elongated along the *c*-axis. They possess well-defined crystallographic faces consisting of the natural cleavage of ZnO with wurtzite structure (zincite) that is a basal (pedion) polar oxygen plane (00-1), a top tetrahedron corner-exposed polar zinc (001) face as well as low-index faces (parallel to the *c*-axis) consisting of nonpolar (-100) face (and  $C_{6v}$  symmetric ones). The "low-symmetry" nonpolar faces, with three-fold coordinated atoms, are the most stable ones, the polar ones being metastable. Additionally, there is no center of inversion in the wurtzite crystal structure, and therefore an inherent asymmetry along the *c*-axis is present, which allows the anisotropic growth of the crystal along the [001] direction. Such materials allowed the theoretical and experimental studies (at real scale) of the relation between the electronic structure and structural properties as well as the influence of parameters such as size, shape, and surface chemistry on the physical properties of such an important II-VI semiconductors. Indeed, the in-depth study of the electronic structure of ZnO nano- to microstructures was carried out at synchrotron radiation facilities to obtain better fundamental understanding of the nanocrystal morphology on its electronic structure. Polarization-dependent soft X-ray absorption experiments were performed on designed ZnO nanomaterials, and the orbital character and symmetry [45] of the conduction band as well as the bandgap [46] were determined.

Another successful achievement of the purpose-built nanomaterials concept can be found in the generation of large arrays of highly oriented ZnO microtubes [47]. Indeed, by playing chemically on the structural characteristics of the materials and by creating a precipitation and aging medium which takes advantage of the surface metastability of the polar faces and in particular the top (001)-Zn face, one may create highly oriented microtubular-array of ZnO on various (polycrystalline or single-crystalline) substrates by a one-step, template-free, simple and cheap, aqueous synthesis.

The latest ordered nanoarrays created from aqueous solutions following the purpose-built nanomaterials concept was *c*-elongated rutile, SnO<sub>2</sub> nanorod arrays [48]. SnO<sub>2</sub> crystallizes in the space group  $P4_2/mnm$  with tin and oxygen atoms in 2a and 4f positions, respectively. The unit cell consists of two tin atoms and four oxygen atoms. Each metal atom is situated amidst six oxygen atoms, which approximately form the corners of a regular octahedron. Oxygen atoms are surrounded by three tin atoms which approximate the corners of an equilateral triangle. Two of each twelve octahedral edges are shared with other octahedra. Edge sharing is symmetrical and opposed in rutile structure. The octahedra are sharing edges and form linear chains along the *c*-axis. The octahedral chains run parallel to the *c*-axis and combine by sharing two opposed edges per octahedron. Each such chain is surrounded and cross-linked to four identical octahedral chains twisted at 90° to the first chain. Adjacent chains are all staggered *c*/2 by the 4<sub>2</sub> screw axes that are oriented along tunnels parallel to *c*. Consequently, the highest electron density parallel to the *c*-axis is observed as well as high polarizability and birefringence. The low index (110) face is the thermodynamically most stable bulk termination and possesses the lowest surface energy. Such stoichiometric surfaces, in which one-half of the surface cations are five-fold coordinated with O ions and the other half are six-fold coordinated because of the presence of a row of bridging oxygens, yields tin atoms with the formal +IV oxidation state. Thus, surface and bulk have similar resistivity. This surface has no net dipole moment in the [110] direction and is therefore a nonpolar surface. Additionally, this centrosymmetric structure of low axial ratios reduces substantially the probability of anisotropic growth of the crystal along the *c*-axis. For such a reason, SnO<sub>2</sub> nanorods and nanowires seldom grow along the *c*-axis but rather along the [101], [301], [200], or [11-2] directions. However, by allowing chemically a slow generation of small nuclei as well as a slow heteronucleation

and growth at low interfacial tension conditions (thermodynamic stability), stable anisotropic (*c*-elongated) nanocrystals with square cross-section and exhibiting the stable (110) faces (according to crystal symmetry elements) may be generated. Indeed, by slow thermohydrolysis of acidic aqueous solutions of tin chloride salts and urea, highly oriented nanorods should grow at normal incidence onto the substrate surface. The typical crystal habit exhibits a two-square base, that is, (001) faces as well as (110) faces (parallel to the *c* axis).

Besides the great stability of (110) faces, it is well known that such a surface provides the best efficiency for the chemisorption and dissociation of oxygenated compounds at the SnO<sub>2</sub> interface due to the lowest interatomic distances between tin atoms (compared to (101) and (111) faces). Such particularity is of crucial importance to improve the current efficiency of SnO<sub>2</sub> catalytic and sensor devices. Given that the exposed prismatic faces of the nanorods are the most stable and nonpolar (110) faces, such a unique morphology confers to these arrays great capabilities to develop innovative and efficient nanosensors. For instance, better sensitivity and selectivity is foreseen due to the optimized exposed faces as well as a fast response (i.e., lower latency time due to their direct growth onto various substrates), their perpendicular orientation (i.e., direct electron pathway), and their anisotropy along the *c*-axis, which provides the highest electron density.

## PERSPECTIVES

Major future developments of the *purpose-built* nanomaterials concept will include refinements of the interfacial thermodynamics model to structural dependent models as well as the essential combination of the simplicity of the aqueous chemical route to economically build well-defined and -ordered nanostructures at low temperature and large scale with the ability of organometallic syntheses to produce controlled multi-elemental and doped structures to achieve true complex nanocomposites of atomically designed functionality. Materials chemistry will definitely play a key role in the fundamental understandings of nanoscale matters and in the proof of concept and development of practical nanodevices.

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