Purpose-built metal oxide nanomaterials. The emergence of a new generation of smart materials*

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Abstract: A new concept has been developed in order to achieve a new generation of smart materials, namely *purpose-built materials*, modeled and designed to match the physical and structural requirements of their applications. A model based on the thermodynamic monitoring of the nucleation, growth, and aging process of metal oxide by minimization of the interfacial tension, yielding to the thermodynamic stabilization of the system, results in well-designed and well-ordered nanostructured materials with the required porosity, morphology, size, and orientation on various substrates.

INTRODUCTION

The ability to control the particle size and morphology of nanoparticles is of crucial importance nowadays both from a fundamental and industrial point of view, considering the tremendous amount of high-tech applications of nanostructured metal oxide material devices such as dye-sensitized solar cells [1], displays and smart windows [2], chemical [3], gas [4] and biosensors [5], lithium batteries [6], and supercapacitors [7]. Indeed, further development, improvement, and optimization of such devices will be reached provided that better fundamental understanding of their fascinating and unique physical properties and electronic structure where quantum mechanics prevail [8] will be available, as well as a better match between the materials design and the required device applications for the sake of miniaturization and performance.

In almost all applications of nanomaterials devices, fabrication represents one of the most important challenges to their realization and commercialization. Indeed, to fulfill the great promise and expectation of nanomaterials, scientists and chemists in particular have developed a plethora of new synthetic techniques and patterning methods, such as self-assembly [9], mechanochemistry [10], chemistry by microwave [11], lithography [12] or template- and membrane-based synthesis [13]. However, to afford the production needs of cheap, clean, reliable, and durable materials with controlled properties for realistic and practical applications of nanotechnology, the request of mass production of thin film devices will probably represent one of the most important issues of the development of future devices. Chemical design of nanomaterials [14] would probably contribute to a great extent. Another crucial issue of nano-scale materials production is the ability to control the purity of the materials.

Achievement of these highly challenging goals will require the ability and the competence to control the thermodynamics and kinetics of nucleation, growth, and aging phenomena involved in the synthesis step. Indeed, controlling the crystallographic structure and the arrangement of atoms along the surface of a nanostructured material will determine most of its physical properties, since most of the atoms are at the surface, due to the characteristically high surface-to-volume ratio of nanostructured materials. Therefore, the ability to tune, enhance, and optimize the material's physical properties is achievable by molecular manufacturing and materials design and will enable the fabrication of novel

devices designed for their applications. Designing materials with desired orientation and faces will be of great importance in order to optimize their properties or even develop new ones.

Here, we would like to introduce a new concept, i.e., purpose-built metal oxide nanomaterials, well sustained by a thermodynamic model of the interfacial tension control which allows the design of a new generation of material with controlled morphology. The basic ideas, as well as some of the achievements, of this concept will be covered in the present overview.

BACKGROUND

The basic idea of purpose-built nanomaterials is to model and design materials with the proper morphology, size, shape, and texture in order to probe, tune, and optimize the investigated physical properties. The purpose is to demonstrate that the same material (crystallographic structure and composition) designed in the proper fashion may achieve better performance, overcoming its weakness or even developing new properties. In our view, the most pertinent parameter to assess and control the design of such a material is the interfacial free energy (γ) of the system. A model based on Gibbs' adsorption equation attempts to quantify the variation of the interfacial tension with the chemical composition of the interface and the dispersion conditions [15]. Proton (or hydroxyl) ions surface adsorption increases the surface-charge density, yielding to the lowering of the water–oxide interfacial tension of the system. At maximum surface-charge density, i.e., when the surface is electrostatically saturated, the interfacial tension is expected to drop sufficiently, allowing the system to attain thermodynamic stability. Assuming a zero interfacial tension at equilibrium by analogy with microemulsions systems where very low surface tension at equilibrium has been reported [16], a quantitative treatment is obtained, yielding to the stability conditions of the system [17]. In the stable area, limited by the point of zero interfacial tension (PZIT), the particles are foreseen to be stabilized, and, consequently, secondary growth phenomenon such as Ostwald ripening is unlikely to occur. Therefore, the size of the particle is expected to be directly related to precipitation conditions such as pH and ionic strength. Concerning the nucleation and growth process that regulates the precipitation of solid phases in solution, the free enthalpy of nucleation shows a maximum as a function of the particle size, which depends on γ^3. Therefore, reducing the interfacial tension should lead to an important lowering of the nucleation energy barrier yielding to the reduction of the particle size. A large stage of nucleation of very small particles is predicted with a very short stage of growth. The particles' size and their distribution are expected to decrease. The results on aqueous precipitation of magnetite (Fe_3O_4) has shown [18] that thermodynamic stability of nanoparticles may be achieved and that the average particle size may be monitored over an order of magnitude showing narrow size distribution. The excellent agreement between theoretical modeling and experiments yields strong evidence for a general efficient growth control of metal oxide nanoparticles under low interfacial tension conditions and draws great expectations for future development of nanomaterials and optimization of their physical properties. Moreover, when thermodynamic stabilization is achieved, not only the size is tailored, but the shape, as well as the crystallographic structure, may be controlled. Therefore, designing appropriate material to match the requirement of its application is possible. For instance, at low interfacial tension, the particle shape does not need to be spherical; indeed, nanoparticles are often spherical to minimize the surface energy because the sphere represents the smallest surface for a given volume. However, if the synthesis or dispersion conditions are suitable (i.e., yielding to the thermodynamic stabilization of the system), the shape of the crystallites will be driven by the symmetry of the crystallographic structure, and, therefore, anisotropy may be easily developed. Manipulating and controlling the interfacial tension enables the growth of material with various orientation and shape required for its applications. Applying the proper solution chemistry to the investigated transition-metal ion, using the natural crystallographic symmetry and anisotropy or by forcing the material to grow along a certain crystallographic direction by chemically

controlling the nucleation, growth, and aging process, develops a new crystal anisotropy.

Recent model refinement and novel development for thin-film processing [19] has been achieved in order to grow material at low interfacial tension allowing the design of nanostructured thin films with controlled morphology, orientation, and size of crystallites and the overall film texture on various substrates, including conducting tin oxide glass, Si wafers, sapphire, polypropylene, or Teflon FEP [20]. The materials currently investigated are wide-bandgap transition-metal oxides such as TiO_2, ZnO, Fe_2O_3, as well as metallic oxides such as RuO_2 and IrO_2.

ACHIEVEMENTS

The first task and successful achievement of this concept has been to develop hematite nanorods to demonstrate that the hematite material (αFe_2O_3) was able to withdraw photogenerated electrons in a photoelectrochemical cell. Many authors have tried to develop hematite solar cells in view of their very attractive qualities, such as low bandgap, cost, and nontoxicity. However, the main conclusion has been that bulk or surface recombinations are too high for any practical applications [21]. Recently, the fabrication of porous nanostructured hematite thin film, consisting of nanoparticles of 10–15 nm in diameter, has been reported showing very low efficiency even under monochromatic light [22]. The main conclusion was that once again the recombination processes were too high to allow photogenerated electrons to be collected at the back contact.

In our approach, we tried to develop anisotropic crystallites elongated along the c axis, e.g., where the dielectric constant is the highest and where the diameter of such nanorods would match the minority carrier diffusion length, reported to be 2–4 nm [23]. Therefore, an enhanced charge separation and photoconversion efficiency were predicted. Indeed, the fabrication of a porous photoanode consisting of large arrays of aligned and perpendicularly oriented single-crystalline hematite nanorods of 4 nm in diameter and 500 nm in length, aggregated in a 50-nm-diameter bundle, and grown on transparent doped tin oxide glass, allows better 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 pathway designed for photogenerated electrons heading toward the back contact rather than random diffusion walk through the network of nanoparticles, overcomes most of the electron scattering and recombination processes at grain boundaries and significantly lowers the well-known hematite bulk recombination losses. As predicted, a better withdrawal of photogenerated electrons is achieved, improving the photoconversion efficiency and yielding to a relatively good photovoltaic response and the development of the first iron oxide sandwich-type photovoltaic devices (2 electrodes set-up) giving several hundred $\mu A/cm^2$ under $300 W/m^2$ illumination and about 60% incident photon to electron conversion efficiency (IPCE) at 350 nm. The overall efficiency was about 0.1% [24].

Moreover, 2D electron quantum confinement into such nanorods has been suggested to contribute to the unusual high efficiency of these cells and is currently under investigation by XPS and XAS at synchrotron facilities [25], likewise its peculiar magnetic properties at low temperature.

In the same spirit as the successful iron oxide nanorods, we have been developing large arrays of perpendicularly oriented and fairly well-aligned zinc oxide hexagonal microrod and microtube [26] thin films for gas sensing and catalytic applications. These materials are grown at $1\mu m$ per hour on various types of substrate (for instance, F-SnO_2 glass and Si wafers). Perfect control of the rod length is obtained over 2 orders of magnitude, basically from 0.1 to 10 μm. The electron transport of such material is found to be very efficient, with a very low level of dark current, and almost no losses at the electrolyte/electrode interface are found under illumination by UV light. These microrods are elongated along the c axis and show well-defined crystallographic faces consisting of the natural cleavage of ZnO (Zincite) which, in turn, allows the theoretical and experimental studies (at large scale) of the relation between the electronic/crystallographic structure on the catalytic activity. In addition, funda-

mental studies of the influence of parameters such as size, shape, and surface chemistry (e.g., polar vs. nonpolar surface of ZnO) may be taken into account.

An interesting variant of ZnO microrods, which also demonstrates the control achieved by this concept, is the flower-like ZnO material produced by limiting chemically the number of nuclei that allow twin planes to develop from where the rod-like structure will grow. Such unique purpose-built materials, imitating the open corolla structure of flowers, combines the advantage of large surface area for light harvesting at various incidence and effective charge carrier generation and transport processes [20].

A great deal of attention will be given to such materials for gas sensors applications due to the well-known surface conductivity of ZnO. These recent advances in the development of nanostructured devices may greatly improve their physical properties due to the ability and the competence to tailor and control the microstructure and surface chemistry at the atomic level and therefore reach a better understanding of their effects on the complex gas surface reaction processes. This will most probably lead to the development and commercialization of nanostructured sensors with significantly improved properties in selectivity, specificity, sensitivity, and reactivity for gas and chemical sensors.

Another achievement has been obtained in the field of electrocatalysis and supercapacitors with the fabrication of purpose-built hydrated RuO_2 materials [27]. Indeed, group VIII metals and metal oxides (e.g. RuO_2, IrO_2) are extensively studied for research and development of electrocatalysts for chlorine, oxygen, or hydrogen evolution for fundamental and applied purposes and represent important energetic, economics, and environmental issues of the chemical industry. However, their stability against corrosion and passivation at high current density and applied bias is problematic. Therefore, in the last decade, mixed oxide materials from group VIII and groups IV and V, for instance, have been developed to improve the corrosion resistance of the electrodes. However, the electrocatalytic activity seems to be very dependent on the chemical composition of the material and very sensitive to the contamination emerging from the synthesis processes. Further technological improvements will contribute to development of more reliable and durable devices. As far as the performance is concerned, the most significant breakthrough will occur from a better fundamental knowledge of the correlation between the surface composition and the electronic structure of the material and its electrocatalytic activity, as well as from a better understanding of the mechanisms and kinetics of the electro-oxidation processes. The key to obtaining such issue will originate from materials science development of novel and smart materials.

To fulfill the needs of stability and performance and to study the effect of high surface area and porosity on the electrocatalytic activity, a new type of electrode material has been developed by our group. This material consists of thin films of amorphous hydrated nanostructured ruthenium dioxide supported on nanostructured ruthenium and deposited on a chemically inert and flexible substrate such as Teflon (FEP) or polypropylene (PP). The outcome is a thermodynamically stable and porous electrode. Characterization has been carried out by electron microscopy, electron diffraction, XAS, standard- and depth-profile XPS, AC impedance spectroscopy and electrochemical methods showing that the material is clean, without residual chloride, and behaves as a pure resistor following the electron scattering model. Under cycling conditions in acidic medium, the electrodes exhibit high capacity and good stability without noticeable degradation of the performance for supercapacitor and hydrogen storage applications [28], and very promising results are expected for the electrocatalysis of chlorine and oxygen.

PERSPECTIVES

A well-designed and well-controlled morphology definitely represents a significant advantage for modeling the physical properties of the materials. Indeed, fundamental knowledge of the influence of parameters such as particle size, surface structure, film texture on the material's physical properties, and

electronic structure is obtainable. Developing nanomaterials with well-defined faces allows one to carry out experiments on polycrystalline samples at real scale and directly compare them with UHV experiments on single crystals such as high-resolution XPS, XAS, LEED, or ELS, and to quantum chemical calculations.

Model refinement assesses the interfacial tension for each face in order to control the direction of growth and therefore the final shape and orientation of the particles. Indeed, knowing the miller indices allows one to model the surface structure of oxygen and therefore to assess the surface charge per face $\sigma(hkl)$ and therefore through the model, the interfacial tension per face $\gamma(hkl)$. This will represent the most exciting upcoming challenge, that is to say, the development of a structure-dependent model to enable modeling and design, and to quantitatively predict the complete growth of nanomaterials. Another exciting but challenging task will be to test and improve the chemical synthesis and thin-film processing method to the fabrication of mixed oxide such as ferrites or cuprates.

Indeed, few limitations are foreseen, which draws great expectations for future development of novel materials. Most of our work is dedicated to metal oxides, due to their great technological applications, but generalization of the concept to build nanometal materials is foreseen and currently investigated, for instance, for ruthenium. We consider this general concept a powerful and promising tool to control and design suitable, reliable, and cheap material at large scale. We are confident that this concept will contribute to the emergence of a new generation of smart materials and will be an active part of the upcoming era of smart nanodevices.

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