ALL-OXIDE HETERONANOSTRUCTURES FOR SOLAR WATER SPLITTING

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Introduction

A plethora of novel and innovative (hetero)nanostructures for hydrogen generation by solar water splitting are being reported[1]. From an academic point of view, any functioning systems are useful to understand and later exploit the fundamental knowledge of the mechanisms and energetics involved in the water oxidation process but from a practical point of view, enabling a sustainable large scale production and implementation of such a technology, requires others issues to be fulfilled such as fabrication and operating costs, toxicity and long term stability in water upon strong illumination by concentrated solar irradiation[2]. Such crucial necessities imply the use of cheap and naturally abundant chemical elements.

Materials synthesis by chemical methods has emerged as one of the most versatile fabrication techniques for the in-depth study and rational delivery of high purity functional nanomaterials, engineered from the molecular to the microscopic scale at low cost and large scale. The latter attributes make this approach very attractive for industrial applications in energy and electronic. However, there is now a common recognition in all fields that conventional technologies, which attempt to improve the performance of existing materials by further development along the same lines, are reaching their limits. Indeed, with diffusion of these technologies already at substantially 100%, there is little room for further improvement. Innovations which consider the environment are necessary when aiming at even higher efficiency. Given this situation, it is now imperative to develop novel multifunctional materials which can produce novelty from the most upstream processes with the aim of realizing a sustainable society. The necessity of materials development which is not limited to materials that can achieve their theoretical bulk limits, but makes it possible to raise those limits by changing the fundamental underlying physics and chemistry is the key to enhanced efficiency and device optimization.

The strategy and major innovation of this research is the ability to develop novel metal oxide semiconductor heteronanostructures consisting of highly pure quantum dots and quantum rods entirely made from aqueous chemistry with controlled surface chemistry[3] and having intermediate bands for ultra-high energy conversion and highly quantized band structure for bandgap and band edge engineering. Such unique characteristics, combined with in-depth investigation of their electronic structure, optical, structural and transport properties by low cost and clean synthetic method provide a substantial advance and revolutionary prospect in the field of semiconductor technology and materials for energy conversion. Such advanced knowledge of the electronic structure and structural properties allows direct implication for fundamental understanding of the energetics and structure-property relationships as well as efficiency optimization of new nanodevices.

Experimental

Materials synthesis. The fabrication of all-oxide highly oriented heteronanostructured arrays of large physical dimension consists of heating homogeneous aqueous solutions of metal salts in the presence of a substrate (e.g. transparent conducting oxides (TCO), glass, coated glass, Si/SiO$_2$ wafers, sapphire, polypropylene, PTFE, Teflon etc) at moderated temperatures (below 100°C) in a closed vessel[4].

In addition, since no organic solvents or surfactants are present, the purity of the materials is dramatically improved. Any residual salts (from the precursors decomposition and/or from the added ionic strength) are easily washed away by water due to their high solubility in aqueous solutions. In most cases, no additional heat or chemical treatments are necessary, which represent a significant improvement compared to surfactant, template or membrane based synthesis methods. A full coverage of the substrate is obtained within few hours (and up to a couple of days in certain cases) provided that the heat capacity of water and surface coverage control are achieved by monitoring the synthesis time in the early stages of the thin film growth. Partial coverage is obtained within the first hours, which may be necessary for certain applications to adjust and tune the overall physical properties of devices (e.g. optical properties of multi-bandgap thin films). The development of multilayer thin films of various morphologies and/or of various chemical compositions – i.e. composite, multi-bandgap, and doped thin films is utilized to create new structures. The complete architecture may thus be designed and monitored to match the requirements of the applications[5]. Growing thin layers directly from the substrate does substantially improve the adherence and the mechanical stability of the thin film compared to the standard solution and colloidal deposition techniques such as spin and/or dip coating, chemical bathing, screen printing, or doctor blading. Scaling-up is easily feasible to produce large scale oriented arrays of most transition metal oxides from aqueous solutions at low temperatures. Highly oriented quantum rod-based metal oxide heteronanostructured arrays have been fabricated using this simple and clean technique.

Electronic structure. In-depth investigation of the electronic structure of the building blocks (i.e. quantum dots and rods of various sizes, aspect ratio and orientation), the interfaces with TCO substrate and the fully grown heteronanostructures have been carried out[6]. Such studies include (polarization dependent) soft x-ray absorption and emission measurements, as well as energy dependent resonant inelastic x-ray scattering. Both synchrotron radiation based soft-x-ray absorption spectroscopy (XAS) which map the conduction band (unoccupied states) of the materials and soft-x-ray emission spectroscopy (XES) which map the valence band (occupied states) on a variety of (hetero)nanostructures have brought important information on bandgap, Fermi energy, work function as well as other band edges characteristics. With high resolution monochromatized synchrotron radiation excitation, resonant inelastic x-ray scattering (RIXS) has emerged as a new source of information for electronic structure and excitation dynamics of nanomaterials. The selectivity of the excitation, in terms of energy and polarization, has also facilitated studies of emission anisotropy as well as for probing the optical transitions in transition metal oxides, especially dd transitions which are dipole forbidden and thus, of very low intensity in other spectroscopies such as electron energy loss spectroscopy (EELS) or UV-vis spectrophotometry. In addition, angle-resolved XAS and XES spectroscopy along with DFT calculation have also been carried out to probe the orbital character and symmetry of the conduction band of important large bandgap semiconductors[6].

Results and Discussion

The study of the size dependence (over two orders of magnitude in diameter, i.e. 2-200nm) on the orbital character of the conduction band of anatase TiO$_2$ nanocrystals provided the first experimental evidence (supported by calculated data) of such an effect[7]. Indeed,

the appearance and predominance of unoccupied states derived from the hybridization of antibonding Ti 4s and O 2p band is observed when the nanoparticle size approaches the exciton radius (ca 1 nm). Such extended hydridization of O 2p with Ti 4s compared to narrow directional 3d is of great importance not only from the fundamental point of view of demonstrating a confinement effect in anatase TiO2 nanocrystals but also for device applications. Indeed, such a result is of great relevance for 3rd generation quantum dot and intermediate band solar cells; for photocatalysis where crystal facets, surface states, and s-doping induced by chemical doping play a major roles in promoting surface chemical reactions and visible light-active response; for renewable fuels such as solar hydrogen generation by water splitting and for water and air purification. Indeed, the presence of s-hybridized bandgap states may improve not only the overall carrier dynamics and electron mobility (i.e., by reducing the electron effective mass and electron-hole recombination) but should also contribute to a significant improvement of the overall efficiency of dye-sensitized solar cells by controlling the interfacial electron transfer and reducing the back reaction[7].

Another related study introduced a new transition metal oxide heterostructure containing junctions of iron oxide (hematite) and titanium oxide nanomaterials, which is readily organized in vertical arrays onto conductive substrates by a combination of inexpensive and scalable techniques. The orbital character of the interfacial region was analyzed by soft X-ray spectroscopies, which indicates the presence of a degree of p-d orbital hybridization that is absent from all reference crystals examined[8]. Consideration of spectra relating to the Ti coordination environment suggests a structural relationship is established between the phases. The confirmed existence of Ti 3d electrons in the interface suggests the new hetero-nanostructure resulted in spontaneous electron enrichment and thus possesses a unique electronic structure, which likely translates to new emergent electronic properties. These macroscopic system properties are currently under investigation in our laboratories. It is foreseen that this fabrication strategy and the resultant novel materials will open new avenues to engineer the electrical and optical properties of transition metal oxide hetero-nanostructures, to specialize structures for critical applications of oxide electronics, most notably those for solar fuel generation and photovoltaics[8].

The electronic structure of another important interface for a number of (opto)electronic devices, that is the TiO_2-SnO_2:F interface, was also investigated by XAS[9]. Its distinct interfacial electronic structure has been established by contrasting spectra with those for anatase and rutile TiO_2, SnO_2:F, and the ZnO-SnO_2:F and CdO-SnO_2:F interfaces. The Ti 3d band of the interfacial oxygen 1s absorption spectrum indicates a reduction in the degree of p-d hybridization and an alteration of the TiO_2 crystal field. Titanium 2p absorption spectra provide evidence for distortion of long-range order around Ti ions in the interfacial TiO_2. These observations can inform methodology to address operational deficiencies associated with the TiO_2-SnO_2:F interface in optoelectronic devices. For example, a comprehensive characterization of the chemically resolved interfacial electronic structure provides information that facilitates the elimination of unfavorable processing conditions, including high temperatures, which are associated with additional costs and diffusion effects between phases, and which preclude the use of inexpensive temperature-sensitive substrates. The results indicate that in solar cell operating conditions, the quasi-Fermi level of electrons in the interface will differ from predictions based on bulk oxide material properties. The interfacial electronic structure in addition influences the electrostatic potential distribution at the oxide-TCO interface, which is often a critical operational aspect of working optoelectronic devices. The description of the unoccupied electronic states at the TiO_2-SnO_2:F interface provided additional information toward explaining deviations in solar cell performance metrics from those expected by bulk material properties and the various predictive models[9].

Finally, we also recently studied experimentally by XAS the interfacial electronic structure origins of losses in α-Fe_2O_3 electrodes and the cause of the widely reported order-of-magnitude photoanodic current increase upon short high temperature annealing[10].

Conclusions

Performance in modern optoelectronics is increasingly reliant on the efficiency of interfacial processes, which are directly influenced by the character and occupancy of electronic states near the interface. The interfacial regions of heterostructures, which can extend several nanometers beyond their actual atomic interfaces, can be characterized by abrupt or gradual changes in chemical, structural, and electronic properties. The nature of these atomic- and molecular-level interactions is not restricted to academic interest; the macroscopic performance of modern technologies is often reliant on their presence. Solar energy conversion devices in particular require these gradients to establish the driving force for photo-excited carrier separation in non-equilibrium (operating) conditions. The chemically resolved electronic structure of such interfaces must be understood on a fundamental level in order to optimize future devices to accommodate strict requirements, which place limits on toxicity and cost. We showed that, as for solar cells and oxide electronics, interfacial electronic structure, surface chemistry and quantum confinement effects are critical factors to control for the high performance of oxide photoanodes for solar-driven water splitting and production of chemical fuels in photoelectrochemical cells.

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