

Ab-initio Simulations in order to improve processing of Nanoceramics

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Nanomaterials have been classified into inter- and intra-nanomaterials, but recent research projects focus on single molecules, like polymeric side chains or atomic monolayers. In these nano-dimensions the manufacturing becomes expensive and even characterization is a challenge. Hence, simulations are necessary to understand and optimize the properties of ceramic materials in terms of powder shape, crystals or at interfaces. The *ab-initio* calculations need no adjusting parameters and calculate the electron wave function in the potential of the atom core. The calculations presented in this overview paper are performed with the DvX α method focussing on three examples and show how these calculations of the electronic structure can be used for improving the ceramic processing. The first example considers how the electronic band structure of nanoparticles changes as a function of the particle size. The second example considers the substitution of atoms in an electro-ceramic material. The last example shows, how the organic macromolecule Eosin on top of a crystalline ZnO surface is bonded, which is important to increase the efficiency of solar cells or photo-catalytic reactions.

Key words: Nano-size effect, Pyrochlore structure, Conductivity, DvX α calculation, Interface structure.

Introduction

Recent progress in experimental techniques allows the processing of advanced materials on an atomic scale. Understanding of the interatomic bonding is the key to manufacture advanced ceramic materials. The forces between atoms can be divided into metallic, ionic and covalent bonding (Fig. 1a) due to the interaction of the electronic wave functions in the electronic orbitals. Metals with their small lattice constants have an overlap between the conduction and valence bands (Fig. 1b), semiconductors and ceramics have a band-gap between them. Polymers and organic materials have covalent bonding with shared electrons. Historically the processing of materials started by alloying metals, ceramics or polymers (Fig. 1c) with species from their own type (Fig. 1d). In the middle of the last century the mixing of different sorts of materials started, for example the addition of ceramic dispersoids into metal melts or the deposition of polymer paints for corrosion protection (Fig. 1e), metallic gold contacts and semiconductor films on electronic devices or the Langmuir-Blodgett type of layered polymers. At the end of the last century, when new sintering techniques were available, advanced microstructures (Fig. 1f), like functional gradient materials (FGM), precursor-derived ceramics or surface coated powders were available. The challenge

of this century is the manufacturing of nano-materials, which have been classified into inter-, intra-, or nano-nano-materials [1], whether second phase nano-particles lie between or inside of primary particles or are equal in size. Recent research has already reached atomic scale and materials are designed on a molecular level (Fig. 1g). For example carbon-nano-tubes containing metallic nanoparticles grow on metallic surfaces, the slurry of ceramic powders contains polymeric surfactants, or photocatalytic polymer films allow the controlled growth of ceramic layers with nano-dimensions [2]. The control of the interfacial parameters becomes important [3] and finding the best material for the required application needs an understanding of the electronic properties.

The most successful physical theories use analytical expressions for describing a physical phenomenon. However, such a theory is not available for material science, because e.g. in a composite material so many interactions occur, that they cannot be described in one formula. Therefore, it is necessary to perform numerical simulations by computer, which have a certain discreteness in time and space, and the evolution of the system is subdivided into steps between each particle or steps on the time scale. The costs for calculations become cheaper and cheaper, whilst for experiments more and more expensive. There are also other reasons, which make it worthwhile to do simulations, like the collection of data in a data-base by extrapolation or extension, where experimental data are missing. Industrial companies use simulation on a macroscopic scale in order to extrapolate laborious experiments to a large

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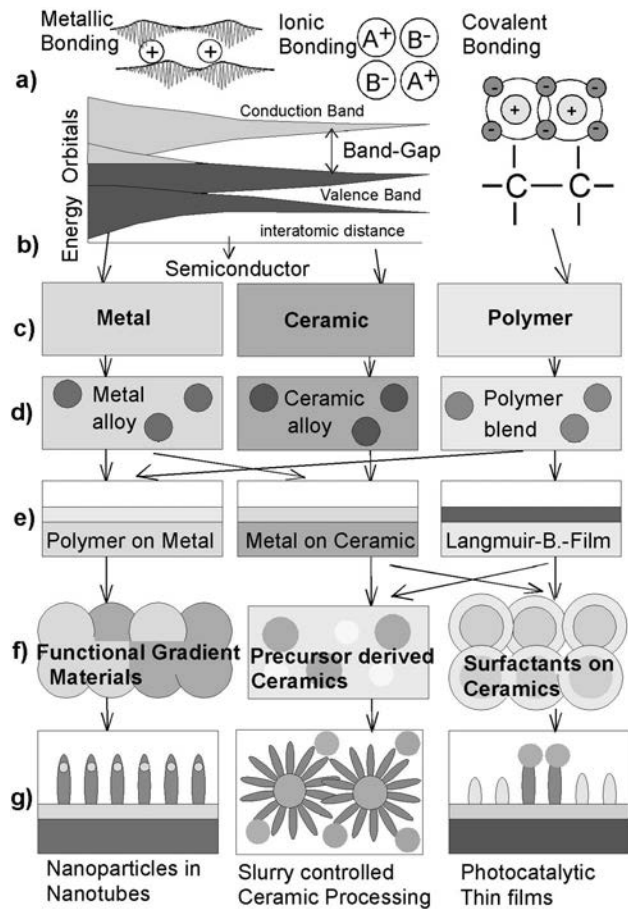


Fig. 1. Basics of material engineering and development of microstructure, (a) the three main types of inter-atomic bonding, (b) their electronic structure, (c) the three main types of materials, (d) simple composite materials of the same material type, (e) composite materials of different types in layered shape, (f) composite materials on a mesoscopic scale in various shapes, (g) some of the contemporary advanced composite materials on a molecular level.

scale, the so-called up-scaling. Finally, simulation is the stimulation for new research and it is a challenge to find new materials faster than by experiment. Each simulation is an approximation to the reality with a certain range of validity. The reliability, which means the confidence in the calculation results, has been improved as computers have become faster and faster and the number of atoms in the calculation has increased. The most accurate calculation methods are the *ab-initio* calculations without assumption of any parameters from experiment (Fig. 2), but more than one hundred atoms is still a challenge. The Molecular Dynamics (MD) method uses empirical potentials between the atoms with less reliability. It has become common, to combine different calculation methods on different length scales and transfer the data interactively between them.

There are many materials science problems worthy of calculation on an atomic scale. One of the most important ones is the surface or interfacial structure and

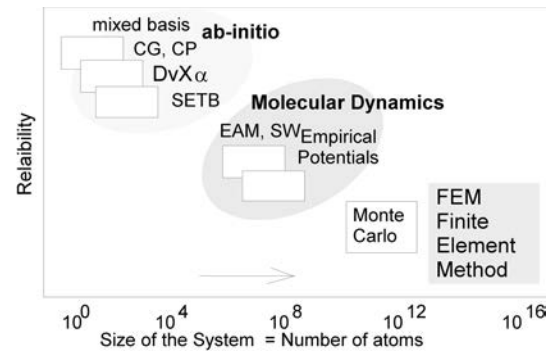


Fig. 2. Calculation methods for material science depend on the size of the system and have different reliability.

their electronic states, since there is a great potential for developing new functional materials and the experimental analysis on an atomic scale is difficult [4-10]. The segregation of impurity elements at grain boundaries has also a great effect on mechanical properties [10]. When crystalline thin films are deposited on substrates, misfit dislocations occur and can destroy the good electrical properties [11]. In the case of composite materials for high temperature applications, mainly particles are embedded in a matrix. In this case also the interface, the volume fraction, morphology, and microstructure play an important role in the properties of the material. As in chemistry the structural analysis of large organic molecules, also for ceramic processing the understanding of the aqueous slurry containing many different materials, additives, binders, surfactants and others needs the support of calculations [12, 13].

This overview paper shows three applications of *ab-initio* calculations for improving ceramic processing, the nano-sized effect, the influence of substituting atoms in a crystal phase and the electronic states at an interface. This paper cannot give a complete description, but can show concepts and directions, in which new calculation research is worthwhile.

Calculation method

The so-called *ab-initio* or first-principle simulation methods calculate the interaction of all electrons in the potential of the atomic cores on a sub-atomic scale. The time-independent Schroedinger-equation $H\psi = E\psi$ is solved numerically for each electron without any empirical parameters or assumptions. The solutions are the wave functions and summation of these intensities leads to the spatial charge density. The calculation methods differ in their grade of approximation and separation of their parameter dependence [14]. Usually atomic movement is excluded and their positions are determined from an experiment or a MD-calculations. The method used in this paper is called the discrete variational X-alpha (DVX α) method and temporarily uses a factor called alpha for the electron density of the core electrons, which is rescaled in every iteration time

step [15]. The solutions, however, are fairly exact with not much difference from the more time-consuming methods and have successfully been applied for material science problems [7, 8]. The software program calculates the interaction of all electrons inside a cluster of about 50 atoms. Outside of the cluster, within a certain radius, the effective charge at the positions of the atoms is considered as a Madelung potential with a range of about 2 nm. When setting the input structure, the charge neutrality should be preserved, since already one additional single electron can change the results. The eigen-values of the wave functions lead to the energy values for each orbital and each energy level is occupied with a certain density. This table can be printed out after the program run and analyzed.

There are several applications of these *ab-initio* calculations, the simplest is the estimation of the band gap. Beneath the Fermi-energy the energy states are occupied and the difference between the highest occupied molecular orbital (Homo) and the lowest unoccupied (Lumo) can be evaluated. The width of the band-gap in between the valence and conduction bands determines the optical or electronic properties, and the doping with different foreign atoms changes the width of the band gap. At grain boundaries usually the band gap gets smaller [5], because the distances to bonding partners change [9]. At interfaces also exited states in between the band gap occur. The plot of the spatial distribution of the charge density is useful to study this change in the interatomic bonding. For example the charge density at surfaces is spread more than 0.5 nm into the vacuum at ceramic surfaces (e.g. MgO) due to the strong ionic character of the atoms. This is important, when the potential between particles and their sintering behavior is considered. The more detailed Mulliken analysis of the electronic charge exchange characterizes the type of interatomic bonding.

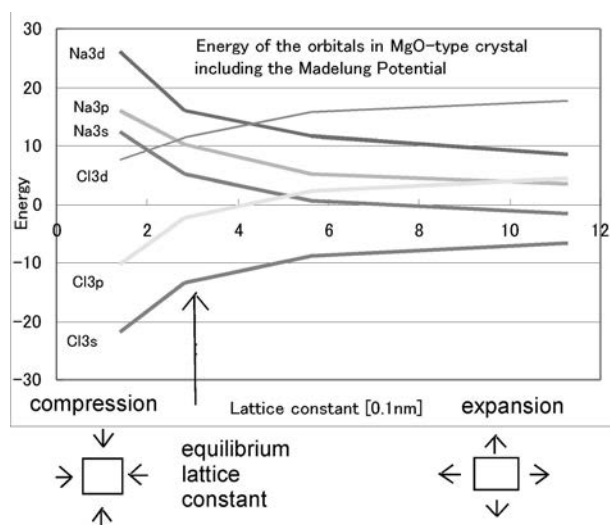


Fig. 3. The energy bands of a NaCl crystal depend on the lattice constants and the bonding energy increases under compression.

When atoms form a crystal, the atomic orbitals transform into molecular orbitals by splitting into bonding and anti-bonding levels and the difference is equal to the bonding energy, which in the case of NaCl is 8.9 eV [16]. Since the electronic orbitals depend on the interatomic distance, they also change, when pressure is applied. The energy of the molecular orbitals as a function of the lattice constant was calculated for a NaCl crystal (Fig. 3). The calculation conditions, like the size of the cluster and the Madelung radius, were the same. With a decrease in lattice constants the splitting into bonding and anti-bonding increases. At the experimentally measured lattice constant the crystal is in equilibrium between the repulsive and attractive forces and has the lowest energy.

Results and Discussion

Nano-size effect at MgO-ceramic particles

Ceramics processing is mainly based on slurries [12, 13], in which raw materials are present in aqueous solution. Chemical reactions in the slurry are liquid-solid or gaseous-solid reactions and are much faster than solid-solid ones with a larger variety of possibilities. The slurry contains besides the crystalline ceramic raw materials, also surfactants, catalysts, enzymes, ions, electrical conducting polymers or insulating polymers and other molecules. In rheology these interaction forces, which occur in the slurry between the particles and molecules, are classified (Fig. 4), for example Coulomb-, polarization-, Van-der-Waals-, steric- capillarity-, adhesion- and hydrophilic- forces. The discrete element method (DEM) [17] tries to find a numerical description of these forces. The electrostatic forces are expressed by the so-called Zeta-potential curve, which strongly depends on the pH value. It is zero at the iso-electric point, where the repulsive and attractive forces are in balance. With this condition the molecules try to arrange in a densely packed manner and often the liquid gel transforms to a solid-like sol. The polarization ability of the particles is the important parameter in these solutions, also the time constant for relaxing an excited electronic state. Since the number of parameters

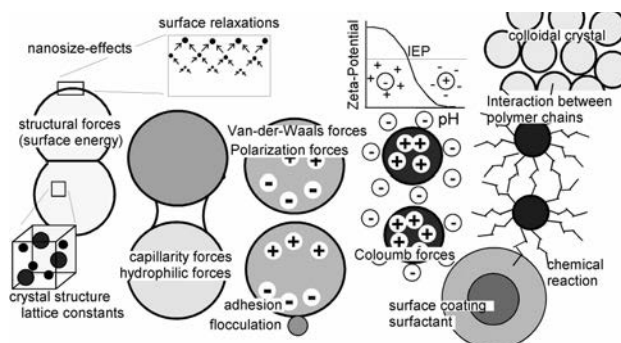


Fig. 4. During ceramics processing many interaction effects occur in the slurry.

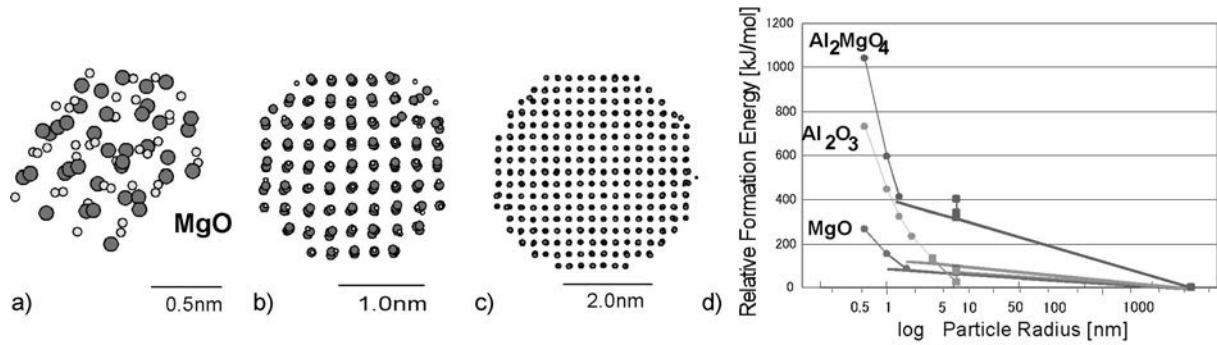


Fig. 5. Surface Relaxations of MgO crystal calculated by MD simulations, (a) 0.5-, (b) 1-, (c) 2 nm-particle (d) enthalpy as a function of the logarithmic particle size.

is larger, the interfacial engineer has more possibilities. The goal of ceramics processing is to adjust the electrostatic forces between the particles, so that they bond together, but also repel each other, so that finally a colloidal crystal is formed. A better understanding is required and the first step in reaching this goal was the calculation of surface energies for three different geometries [18].

When the particle radius reaches nanometer dimensions, three different size-effects occur, relaxation effects of the structure, a change of the electron orbital energy and a change in the polarization ability. Structural nano-size effects are the surface relaxations of the particles, or in the case of sintered nano-materials the thicker grain boundary region compared to the usual polycrystalline materials [19]. The atoms in these regions are weakly bonded compared to the usual polycrystals, and hence, nano-sized materials show special properties. Recent research activities focus on the processing of ceramic nano-particles, as nano-size particles show faster progress of a solid-state reaction, because the diffusion path for the reaction is shorter. On the other hand, the surface relaxations affect almost all atoms in the nano-size particle, as can be seen in the structural plot of MD-calculations for MgO-nano-particles (Fig. 5 a-c). The enthalpy (Fig. 5d) was calculated and the graph shows a steep increase, when the particle size is below 10 nm. The corresponding surface energy is in good agreement with experimental values [18].

The goal of DvX α calculations is to clarify the second nano-size effect, whether the electronic properties change. The cluster size for these calculations was kept constant ($\text{Mg}_{13}\text{O}_{14}$), but the radius of the surrounding Madelung potential was expanded, as shown in the inset of Fig. 6. The O-2s- and 2p- orbitals lie below the Fermi energy and are dissociated into energy bands. As a function of the particle size, the lower energy of the 2p-band shows a small decrease to -4 eV and also the energy of the 2p-band decreases (Fig. 6). When particles with relaxed surfaces, as calculated by MD (Fig. 5 a-c), are used, the lower limit of the 2p-band is further decreased to -6 eV, and the 2p-band is expanded in size. This can be explained by the broadening of the

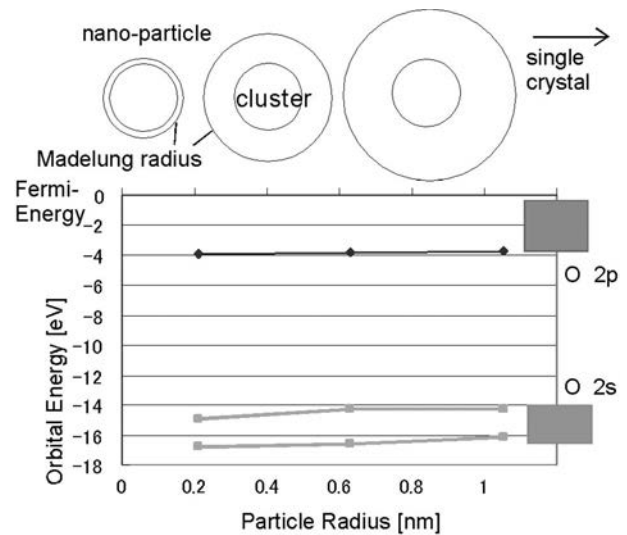


Fig. 6. Effect of the nano-particle size on the O-orbital energy of MgO.

distribution of bonding length due to the surface relaxations. Hence, both nano-size effects change the properties in the same way. The third effect, which is not studied in this paper, leads to a decrease in the polarization ability and can explain the experimentally observed flocculation of nano-particles. These results show, that due to these nano-size effects the electronic properties of nano-particles change and new materials properties arise.

Substitution of Bi in the $\text{Bi}_2\text{Ru}_2\text{O}_7$ phase by other elements

The ceramic phase $\text{Bi}_2\text{Ru}_2\text{O}_7$ and its high-temperature modification $\text{Bi}_2\text{Ru}_2\text{O}_{7-x}$ are considered as substituents for the lead-containing RuO -phases in order to produce environmental-friendly resistor materials. The material is used as a thin film in electronic devices. The substitution of Bi by Pb or Tl in $\text{Bi}_2\text{Ru}_2\text{O}_7$ decreases the resistivity [20] and also the substitution by other elements is considered as a way to manufacture materials with adjusted resistivity [21]. The crystal structure of $\text{Bi}_2\text{Ru}_2\text{O}_7$ is Pyrochlore, where the Bi atoms have cubic coordination, Ru six-fold coordination (Fig. 7a). The lattice

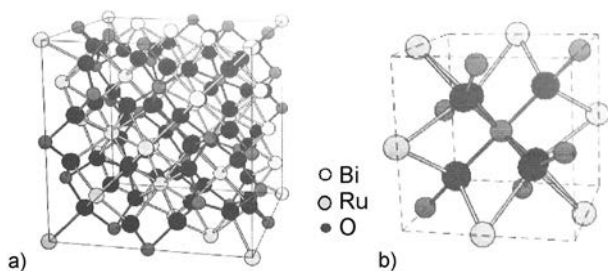


Fig. 7. Pyroclore structure of $\text{Bi}_2\text{Ru}_2\text{O}_7$ (a) unit cell, (b) cluster for DvX α calculation.

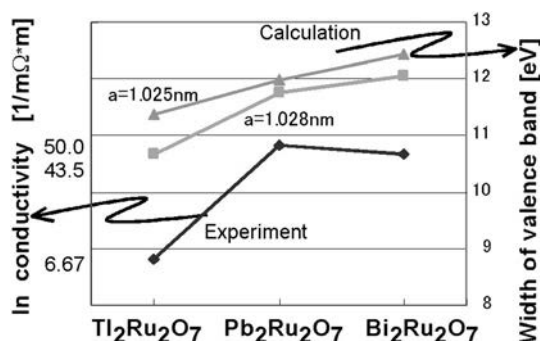


Fig. 8. Logarithmic conductivity in $\text{Tl}_2\text{Ru}_2\text{O}_7$, $\text{Pb}_2\text{Ru}_2\text{O}_7$, $\text{Bi}_2\text{Ru}_2\text{O}_7$ and the width of the conduction band.

constants are $a=1.0252$ nm for $\text{Bi}_2\text{Ru}_2\text{O}_7$, $a=1.0253$ nm for $\text{Pb}_2\text{Ru}_2\text{O}_7$, and 1.0216 nm for $\text{Tl}_2\text{Ru}_2\text{O}_7$, respectively [22]. The electric resistivity for the three phases is $15 \mu\Omega$ m, $2 \mu\Omega$ m, and $2.3 \mu\Omega$ m, respectively [20].

The cluster for the DvX α calculations includes 6 Bi-, 18 O-, and 7 Ru-atoms, one of the Ru-atoms is in the center (Fig. 7b). The Bi was substituted by the elements Tl, Pb, and the calculation using two sets of lattice constants, one for $\text{Bi}_2\text{Ru}_2\text{O}_7$, which is very similar to $\text{Pb}_2\text{Ru}_2\text{O}_7$, and one for the $\text{Tl}_2\text{Ru}_2\text{O}_7$ phase, were performed to simulate a substitutional solid solution. The results of the DvX α calculations are plotted in Fig. 8 as the width of the valence band, estimated by the energy difference between the lowest band orbital in the valence band and the Fermi energy level. This width is a measure of the number of charge carriers and, hence, of the electric conductivity. Indeed the experimentally-measured values for the conductivity, which were converted from the above mentioned values of resistivity [20], show the same increase for the three phases (Fig. 8). Hence, the calculated width of the valence band can be used in this simplified assumption to predict the conductivity of these ceramic alloys, although the conductivity depends on many other factors as well. The decrease in the lattice constants from 1.025 to 1.028 nm (Fig. 8) increases the conductivity as expected from the band structure, but the effect is small, which implies that the mutual substitution of those elements in a solid solution is appropriate for adjusting to a desired value of the resistivity. Also other calculations on crystalline interfaces of composite

materials make sense, but in this paper we proceed in the following to an example of an organic/ceramic interface.

Atomic bonding between an Eosin molecule and a ZnO surface

Organic molecules suitable for ceramic processing are those with reactive groups, for example Sebacic acid with its two acid groups can be successfully used for aqueous processing of AlN [23]. The second requirement for advanced ceramics processing is the self-organization of the polymer molecules, which means the ordering of molecular chains e.g. by weak Van-der-Waals forces. This phenomenon can be used to produce self-assembled monolayers (SAM) [2], which means monolayers, which are ordered by molecular forces. These organic molecules can have several functions: 1) They are templates for further bonding or structuring the ceramic particles, either on a flat substrate or on a round particle to maintain the distance between the particles. 2) They are directly used as precursors, which means during burning they get oxidized, the carbon chains are removed and the material transforms to inorganic ceramics. 3) The efficiency of solar cells or photo catalytic reactions can be enhanced, when organic dyes are bonded in an optimized way to the ceramic surface [24, 25]. The excited electrons can pass through the interface with a higher efficiency and a lower recombination coefficient, when the electron transfer at the interface is optimized. The geometry and location of the bonding has an influence on the electronic orbitals as evaluated from the calculations, but the preparation, separation and even the characterization of the polymer molecule orientation are still challenges.

The organic macromolecule Eosin (Fig. 9) consists of three aromatic rings, where in the middle ring one of the C-atoms is substituted by O, and with a fourth benzol ring on top. The ligands consist of four Bromide atoms, and a COONa-group on the upper Benzol ring. The bonding length and angles are optimized to the lowest energy configuration using the force field of the HyperChem software. The upper Benzol ring and the C=O double bond are always parallel, and this plane rotates perpendicular to the lower three-fold Benzol-ring. The bonding to the (10.0) ZnO-surface (Fig. 10) is performed by substituting the Na ion through a Zinc

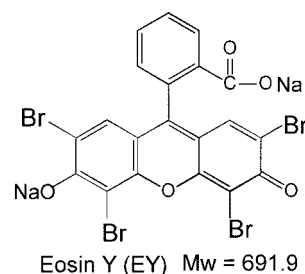


Fig. 9. Organic molecule Eosin Y with its molecular weight.

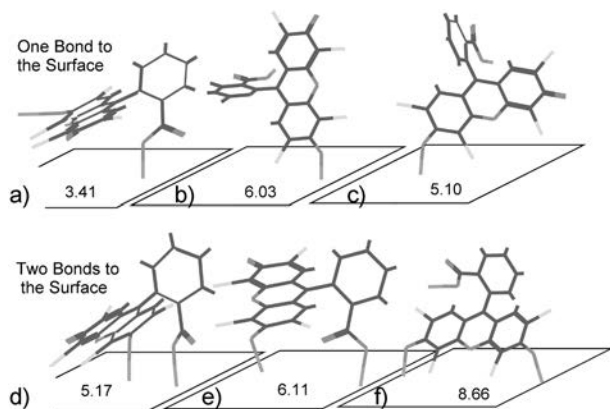


Fig. 10. Possible arrangements of a Eosin molecule on a ZnO surface, the number is the relative energy of the organic molecule.

atom from the ceramic surface. In the experiment the following cases can be realized by selective substitution of the Na atom in an intermediate step by a Sulphate group, which reacts with the ZnO surface. The bonding can be performed by a single bond (Fig. 10a-c) or via double bonds (Fig. 10d-f), whether one or both Na atoms are substituted. The two cases in Fig. 10b and c are chemically identical, but the geometry of the bonding angle towards the crystalline interface is changed due to the rotation of the molecule. The case 10(f) is unlikely to occur, because it requires the breaking of the C=O double bond and changes the chemical nature of the molecule. The structural energy for this case is the highest as indicated by the numbers in Fig. 10. The cluster for the DvX α calculation of the Eosin/ZnO interface consists of the 37 Eosin atoms and O- and Zn-atoms, seven each, from ZnO. The symmetry subroutine of the program reduces the number of non-equivalent atoms, so that in total about 120 wave functions were considered. The Coulomb charge of about 500 other bulk ZnO-atoms are included in the Madelung potential, so that the wave functions in the cluster are realistically treated as if there is a crystalline ZnO surface environment. For comparison it is impor-

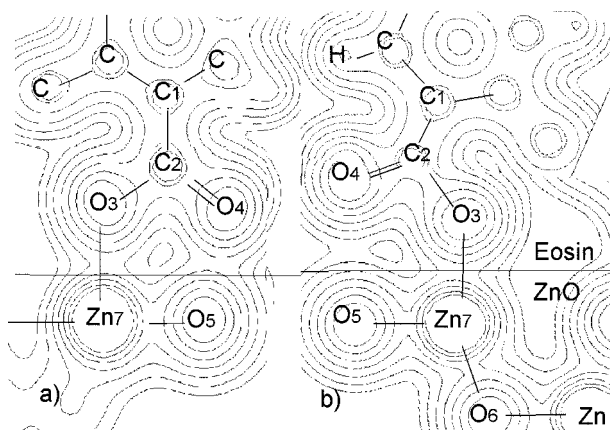


Fig. 11. Charge density calculated by DvX α method; the geometrical model in (a) refers to fig. 10(a), in (b) to fig. 10(d).

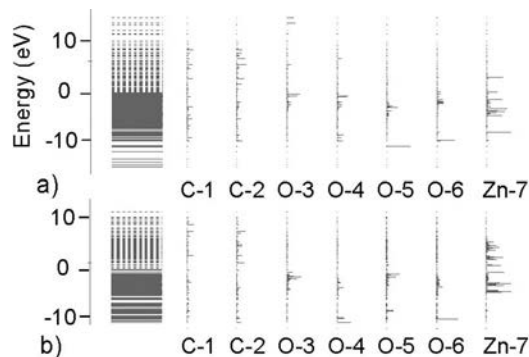


Fig. 12. Energy orbitals of Carbon (C), Oxygen (O) and Zn (Zn) at the Eosin/Zincoxide interface, the configuration and atom numbers in (a, b) refer to fig. 11(a, b) respectively.

tant to keep the number of atoms, their effective charge and bonding length constant.

The results of the calculated charge density maps are shown in Fig. 11(a) and 11(b) in a plane perpendicular to the interface for the two cases, which correspond to the geometry in Fig. 10(a) and Fig. 10(d). The iso-contour lines around the heavy Zn are steeper than at light elements C, or O, and are smeared out in the upper Benzol ring. The bonding between the atoms O-3 of Eosin and Zn-7 of ZnO is about the same in both cases, but the non-bonding atoms O-4 and O-5 are a little closer together in the case of Fig. 11a. The energy of the electronic orbitals is shown in Fig. 12(a, b) where the atomic numbers correspond to those in Fig. 11(a, b). In these plots the y-axis shows the energy, the x-axis the occupancy for T=0 K. Most of the orbitals have the same energy, except that in the valence band of O-3 some additional excited states (hatched lines) appear above the Fermi energy, while the configuration in Fig. 12(b) has a quasi-continuous structure of unoccupied states for the bonding Zn-7-atom about 1eV above the Fermi energy. The reason for this charge transfer can be figured out by the Mulliken population analysis and showed in case of Fig. 12(a) a remarkable charge transfer from the 3p-orbital of Na to the O-3 atom. Both structures (a) and (b) have unexcited states in the Carbon atoms, but (b) has a larger density of states in the conduction band of Zn-7, which should lead to a better performance as a solar cell. The results of these electronic calculations can distinguish the type of bonding and now it is the question to the experiment, which is the best configuration for the desired property? This correlation, a kind of calibration, is the next step in research.

Summary

Using *ab-initio* calculations the electronic orbitals can be characterized and hence, the transfer of excited electrons across the interface optimized. This improves the process of photo-catalysis and the solar cells based on organic/inorganic interfaces. Also the phenomenon

of adsorption of organic molecules on different ceramic substrates can be understood and applied for recognizing and identifying certain substances. By understanding the chemical bonding across the interface, it is possible to manufacture materials with better properties.

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