The Smallest Possible Nanocrystals of Semiionic Oxides

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General bonding principles are used to predict the structure of individual nanocrystals in nanocrystalline materials with semiionic bonding. The relationship between the general principles and actual nanocrystal structures is demonstrated using titanium dioxide in the anatase form. The proposed nanocrystals simultaneously fulfill strict criteria of stoichiometry, high coordination, and balanced charge distribution. The smallest such nanocrystals are remarkably simple, e.g., consisting of less than 100 atoms in anatase. According to computer simulations, these nanocrystals show strong quantum size effects, while other clusters of similar size instead show typical defect characteristics.

Metal oxides are crystalline materials in which a combination of covalent and ionic bonding stabilizes a regular ordering of the atoms.[1] Macroscopic crystals are terminated along characteristic cleavage planes with low reactivity.[2,3] In small clusters, on the other hand, the crystal structure is generally unstable due to the reactivity of dangling surface bonds and strong electrostatic imbalances. Instead, molecular clusters are formed in which the atoms arrange themselves very differently compared to the bulk crystalline structure. Between these two limiting cases, metal oxide materials comprised of clusters with diameters in the nanometer size range, so-called nanostructured materials, exist.[4,5] By careful preparation, the crystalline arrangement of the atoms can be maintained down to cluster diameters in the nanometer range. Nanostructured materials are important in a number of technological applications, such as dense information storage and efficient energy conversion. One important aspect of the nanostructured materials is the greatly enhanced surface area, and e.g., surface energies are important for the thermodynamic phase stability in nanocrystalline materials.[6] There are also fundamental changes to the physical and chemical properties of these crystals with decreasing size.[7] For example, so-called quantum size effects modify band gaps, an important consideration in many electronic applications.[8] It is therefore important to establish the fundamental properties and structural limitations of nanostructured materials. For example, it is not known how small nanocrystals of complex oxides can be made before either the nanocrystals become unstable or they loose their quasi-crystalline electronic properties.

Theoretical investigations of nanostructured metal oxide materials, such as titanium dioxide, suffer from several complications.[9] Many small metal oxide clusters have been accurately treated using standard quantum-chemical methods, but they have usually fallen short of the nanocrystal size range. Clusters have also been used extensively to study bulk and surface properties, but there are frequently severe problems associated with the high surface-to-bulk ratio that demand special attention. Two strategies are commonly used to overcome problems of surface termination in the clusters: saturation of dangling bonds, and embedding to include long-range electrostatic forces. This has made it possible to use relatively small clusters to simulate crystalline bulk and surface proper-

ties.[10] Nevertheless, it is typical for edge effects to drive up the required cluster size to more than 100 atoms.[11] An alternative approach is to construct free clusters based on general bonding principles, such as stoichiometry and coordination.[12]

Here, a general strategy designed to model pure nanocrystals in which both ionic and covalent bonding effects are taken into account is presented. This consists of a set of general criteria to be satisfied by the individual nanocrystals. We consider that the semiionic character of the bonding requires strict criteria of high coordination and balanced charge distribution to be accomplished simultaneously, without resorting to artificial termination by embedding or saturation. Using anatase titanium dioxide as an example of broad interest,[13] we here show that specific nanocrystals predicted by the general principles are surprisingly simple, and display quantum size effects that are characteristic of proper nanocrystals. This contributes to the general understanding of the transition from clusters to crystals with increasing cluster size.

A number of anatase clusters with diameters of about 1 nm have been considered. Atoms were first placed at selected positions consistent with the unrelaxed crystal geometry throughout. The existence of nanocrystals with different atomic arrangements compared to the bulk crystal structures cannot be ruled out, but are not considered further here. Many of the clusters initially generated were discarded due to unphysical coordination of some of the constituent atoms. In the following, we focus on a specific type of clusters that consistently showed outstanding promise in terms of calculated properties. Only *pure crystals* were considered, and thus no saturation of dangling bonds was allowed. Furthermore *no point-charge embedding scheme* was used. To avoid problems of charging, *stoichiometric*, and thus *neutral*, clusters were considered. *High coordination* of all atoms was sought. Specifically, clusters with all oxygen atoms coordinated to at least two titanium atoms, and all titanium atoms coordinated to at least four oxygen atoms, were considered. This is consistent with the general requirement that all atoms should have sufficient coordination to support their formal oxidation state, i.e., O^{2-} and Ti^{4+} in the case of titanium dioxide. The clusters were finally selected to have *no net dipole moment*, an important consideration, e.g., for polar oxide surfaces. In some of the clusters, this could be achieved strictly by using clusters with inversion symmetry.

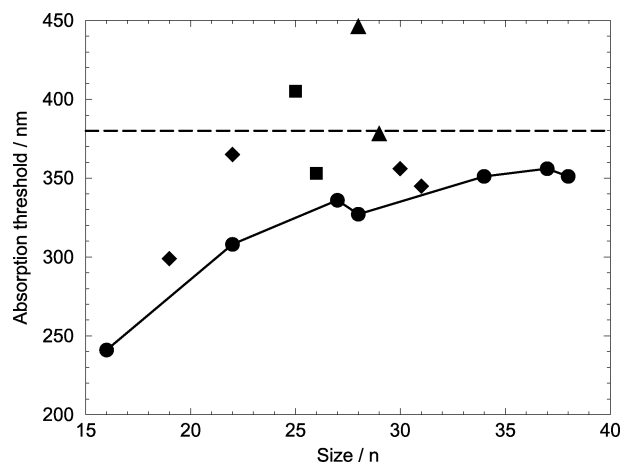Despite the simplicity of the here presented ideas, the

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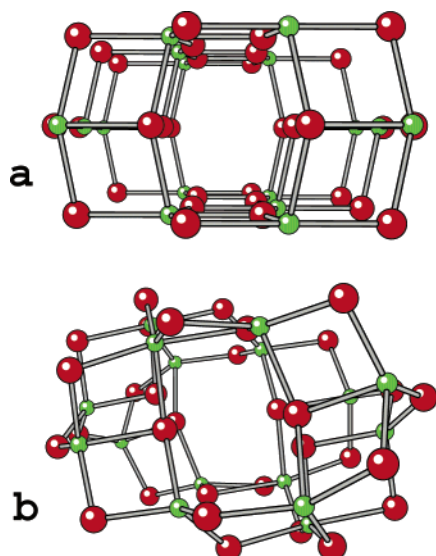
Figure 1. Anatase $Ti_{16}O_{32}$ cluster. (a) Unrelaxed crystal coordinates. (b) Fully optimized structure from DFT calculations with a TZP basis set.

Figure 2. Calculated optical absorption thresholds for unrelaxed stoichiometric anatase nanocrystals and clusters [$(TiO_2)_n$ with n in the range of 16−38)]. The circles represent the nanocrystals fulfilling strict criteria of stoichiometry, balanced charge distribution, and high coordination of all constituent atoms. The diamonds represent the clusters with dipoles, the squares the clusters with 3-fold coordinated titanium atoms, and the triangles clusters with both dipole and 3-fold coordinated titanium atoms. The dashed line represents the experimental absorption threshold bulk limit, corresponding to a band gap of 3.2 eV.[13]

generation of clusters simultaneously fulfilling all the criteria is not trivial. The situation is in this respect more complicated for semiionic materials compared to essentially metallic, covalent,[14] and ionic[15] nanostructured materials in which at least one of the here considered criteria is trivially satisfied. Nanocrystals dominated by either covalent or ionic bonding effects may, in a sense, be seen as the limiting cases in which the requirements of balanced charge distribution and high coordination, respectively, become unimportant. For oxides containing octahedrally coordinated metal atoms, comparatively large clusters must, furthermore, be used in order to achieve satisfactory coordination of all atoms. The strategy employed here was to first generate a large cluster from which unwanted atoms could be removed. The largest cluster ($Ti_{38}O_{76}$) was taken from a previous investigation of dye-sensitized titanium dioxide where it was used ad hoc to model the substrate.[16] Smaller clusters were generated by systematically stripping off stoichiometric units $(TiO_2)_n$ with n typically in the range of 1−3, until the smallest $Ti_{16}O_{32}$ cluster, shown in Figure 1, was reached.

As a first test of the electronic properties of the generated clusters, optical absorption thresholds were calculated for the unrelaxed clusters using the semiempirical INDO/S-CI scheme in ZINDO with a 10 × 10 singles CI.[17] Absorption thresholds provide a sensitive probe of the quality of the electronic structure of the clusters, as structural defects introduce band gap states, with a corresponding reduction of the absorption threshold compared to defect-free materials. Results for a number of $(TiO_2)_n$ clusters with n in the range from 16 to 38 are shown in Figure 2. The results for the clusters with the strictest selection criteria imposed, i.e., simultaneously requiring that all titanium atoms be coordinated by at least four oxygen atoms and that there should be no dipole moment, clearly show systematic quantum size effects, with the absorption thresholds increasing gradually from 240 to 350 nm as the clusters are increased from $n = 16$ to $n = 38$. The absorption threshold starts to level off for the larger clusters, consistent with the approaching of a bulk limit. The calculated value of 350 nm for the threshold of the largest clusters considered here is in reasonable agreement with the experimental value of 380 nm, corresponding to a band gap of 3.2 eV.[13] The accuracy of the calculations is limited by several factors, including the parametrization scheme and the neglect of structural relaxations. Therefore the systematic trend

is more important in itself, rather than the good agreement in terms of actual numbers. In particular, the results show rapid emergence of bulk properties for the unrelaxed nanocrystals. This is useful for cluster calculations of crystal and surface properties.

Results from clusters that do not satisfy all bonding criteria mentioned above are also included in Figure 2. These clusters were also generated by removal of TiO_2 units from larger nanocrystals, but in such a way that they did no longer satisfy all the bonding criteria. In particular, clusters with 3-fold coordinated titanium atoms as well as clusters having overall dipole moments were considered. These clusters all show longer absorption threshold wavelengths compared to the nanocrystals of similar size, in some cases even longer than the bulk value. Thus all bonding criteria need to be considered in order to correctly model defect-free clusters.

The effect of structural relaxations was subsequently investigated for selected nanocrystals. Complete geometry optimizations were performed using density functional calculations, with Perdew−Wang exchange−correlation functionals (PW86x-PW91c) and large core potentials, in the ADF program.[18]

The relaxed structure and electronic properties were investigated in detail for the smallest nanocrystal ($Ti_{16}O_{32}$) by optimization using basis sets up to the triple-ζ with polarization (TZP) level. Already this smallest cluster, which due to its extremely high surface-to-bulk ratio is expected to be the least stable, showed remarkable stability. As shown in Figure 1, there are large local relaxations, but the cluster kept a charge-balanced structure, and all atoms maintained satisfactory coordination, with Ti−O bonds in the range of 1.7−2.3 Å. In other words, the nanocrystal continued to satisfy the strict bonding criteria through the optimization. The density of states for the ADF optimized structure was investigated using the B3LYP hybrid HF-DFT method and the LANL2DZ basis set with GAUSSIAN98.[19] The calculated density of states is shown in Figure 3, where the lack of band gap states shows that the relaxation does not introduce electronic defects. The absorption threshold for the fully relaxed $Ti_{16}O_{32}$ nanocrystal was, furthermore, calculated to be 160 nm, using the ZINDO-CI method as above. This
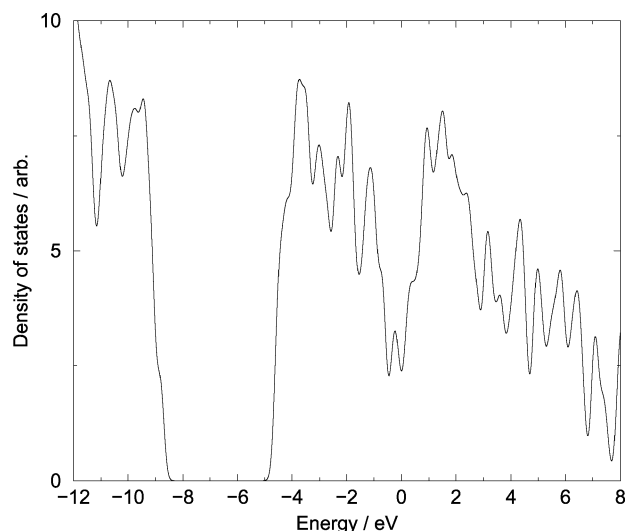
Figure 3. Calculated density of states for the optimized $Ti_{16}O_{32}$ cluster according to B3LYP calculations with the LANL2DZ basis set. The plot includes the upper part of the valence band, the fundamental band gap, and the lower part of the conduction band.

wavelength is substantially shorter than the 240 nm calculated for the unrelaxed structure. The corresponding optical band gaps are 7.6 eV for the relaxed $Ti_{16}O_{32}$ nanocrystal, and 5.1 eV for the unrelaxed $Ti_{16}O_{32}$ nanocrystal, to be compared with 3.5 eV for the unrelaxed $Ti_{38}O_{76}$ nanocrystal and 3.2 eV in the experimental bulk limit.

For some of the larger nanocrystals ($(TiO_2)_n$ with $n = 22$, 28, 34, and 38), the structural relaxations and their influence on the electronic properties were estimated from ADF optimizations using a single-ζ (SZ) basis set. For all clusters, all atoms maintain satisfactory coordination as judged by the same bonding criteria as above. Furthermore, the calculated absorption thresholds for the relaxed structures are all shifted significantly toward shorter wavelengths compared to the corresponding unrelaxed clusters, indicating that the relaxed nanocrystals remain defect-free. The rapid convergence toward the bulk absorption threshold seen for the unrelaxed nanocrystals is, however, suppressed for the relaxed nanocrystals. According to the ZINDO-CI calculations the absorption thresholds for all the relaxed structures fall in a relatively narrow range of about 20 nm around an average value of 155 nm. While a full understanding of the complicated interplay between structural relaxations and the absorption thresholds demands further investigation using better basis sets and a wider range of nanocrystals, the fact that the bulk band gap is approached more slowly for the relaxed nanocrystals is compatible with experimental evidence of appreciable quantum size effects in titanium dioxide nanocrystals up to a few nanometers in diameter.

It is noteworthy from a technical point of view that the electronic structure calculations of the here considered class of proper nanocrystals generally were found to converge easily. Convergence problems are otherwise common in metal oxide cluster calculations, but the criteria used to select stable nanocrystalline clusters appear to have the simultaneous advantage of removing electronic degeneracy problems associated with defects and dangling bonds. This facilitates cluster modeling of bulk and surface properties, as well as theoretical studies of nanocrystals by quantum-chemical calculations.

The smallest titanium dioxide nanocrystal we have found to obey all necessary criteria associated with charge balance and atomic coordination is $Ti_{16}O_{32}$, which cannot be reduced further in size without either abandoning the anatase atomic arrange-

ment, or induce defects in the form of under-coordinated atoms. This therefore represents a theoretical lower limit on the size of anatase nanocrystals. A number of other small nanocrystals are also proposed. These nanocrystals are surprisingly small, considering the structural complexity of anatase. This suggests that it should be possible to produce significantly smaller nanocrystals compared to those that are commonly used today. As demonstrated by the electronic structure calculations, this would extend the range of available quantum-size effects considerably, as such effects are very strong for the smallest considered nanocrystals. Similar results can be expected for many related materials. The particular size for which the desired minimum coordination can be realized will, however, vary somewhat between different crystal forms. The proposed bonding principles are formulated in a general way in order to be applicable to a wide range of nanostructured materials in which both ionic and covalent bonding must be taken into consideration. This includes, for example, several of the II−VI and III−V semiconductors that are also used frequently as nanostructured materials.

In summary, we have found a clear relationship of the structure of defect-free metal oxide nanocrystals to general bonding principles of semiionic materials. This can be summarized in a general rule stating that proper nanocrystals are stoichiometric clusters that have a balanced charge distribution, and in which all the constituent atoms have sufficiently high coordination to support their formal oxidation state. The application of these simple ideas is found to facilitate the prediction of nanocrystal structures considerably. The ability to consider atomistic structures rather than schematic models is an important step toward a better understanding of nanostructured materials, and should thus be valuable both for guiding new experimental efforts to make small nanocrystals, and for further theoretical investigations of the structure and properties of nanocrystalline materials.

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