Electronic structure of nanoscale iron oxide particles measured by scanning tunneling and photoelectron spectroscopies

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We have investigated the electronic structure of nano-sized iron oxide by scanning tunnelling microscopy (STM) and spectroscopy (STS) as well as by photoelectron spectroscopy. Nano particles were produced by thermal treatment of Ferritin molecules containing a self-assembled core of iron oxide. Depending on the thermal treatment we were able to prepare different phases of iron oxide nanoparticles resembling \( \gamma \)-Fe\(_2\)O\(_3\), \( \alpha \)-Fe\(_2\)O\(_3\), and a phase which apparently contains both \( \gamma \)-Fe\(_2\)O\(_3\) and \( \alpha \)-Fe\(_2\)O\(_3\). Changes to the electronic structure of these materials were studied under reducing conditions. We show that the surface band gap of the electronic excitation spectrum can differ from that of bulk material and is dominated by surface effects.

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I. INTRODUCTION

Nano-sized transition metal oxides particles can be expected to show size dependent optical, magnetic and chemical properties with possible applications in catalysis and magnetic and optical devices. It has already been shown, that catalytic and magnetic properties of nanoparticles might be quite different from bulk materials. An example are nano-sized particles of the compound \( \text{Fe}_3\text{O}_4 \), which exhibit superparamagnetism and, at the same time, enhanced catalytic properties compared to the bulk material. The size dependence of the catalytic properties can be associated with an influence of size on the electronic structure of the material. This influence can be due to the surface tension of the particle, resulting in an effective pressure or to changes of the stoichiometry (and resulting changes of the state of oxidation of Fe) of such particles, driven by the large surface to volume ratio.

Here we investigate the electronic structure of nano-sized iron oxide by scanning tunnelling microscopy and spectroscopy as well as by photoelectron spectroscopy and optical spectroscopy. To address the question of stoichiometry and oxidation state the effect of oxidizing and reducing atmosphere on the electronic structure of the nano particles is also investigated. To produce nano-sized iron oxide particles we utilized the ability of Ferritin to self-assemble and construct a core of iron oxide. Ferritin is the major cellular iron-storage protein and consists of a spherical hollow shell composed of 24 polypeptide subunits and is able to store iron as hydrated iron oxide in the internal cavity. The inner and outer diameters of the protein shell are about 8 and 12.5 nm, respectively. The iron core shows a structure similar to that of the mineral ferrihydrite (\( 5 \text{Fe}_2\text{O}_3 \cdot 9 \text{H}_2\text{O} \)). Hydrophilic and hydrophobic channels penetrate the protein shell and provide the means by which iron and other atoms can be accumulated within or removed from the molecules. In previous work, Ferritin was used to prepare several kinds of nanoparticles and nanocomposites. Furthermore, Ferritin molecules inherently show photocatalytic activity.

II. EXPERIMENTAL

Monolayers of Ferritin molecules were prepared by the Langmuir-Schaefer technique. A Ferritin solution (0.15 mg/ml horse spleen Ferritin from Sigma) in 10 mM NaCl with a pH of 5.5 was filled in a commercially available Langmuir-Trough (Nima Technology). A few micrograms of trimethylolactadecylammonium bromide (Fluka) were solved in chloroform to form a concentration of 1 mg/ml and was then spread over the Ferritin solution subphase. After compression to a surface pressure of 30 mN/m and an adsorption time of a few minutes the monolayer was transferred to a freshly cleaved surface of a highly oriented pyrolytic graphite (HOPG) substrate by the horizontal lifting method. Further details of preparation of 2D arrays are described elsewhere.

Prior to the introduction into the ultra high vacuum (UHV) chamber all samples were annealed in air at different temperatures and for different time intervals (~ 575 K for one hour, ~ 675 K for one hour or ~ 675 K for five hours) to eliminate the protein shell and to further oxidize the iron core. After introduction into the chamber the samples were annealed in situ under a 1 \( \times \) 10\(^{-6} \) mbar oxygen atmosphere at the respective temperature for a few minutes. Utilizing this process we produced dense arrays of iron oxide nanoparticles. To vary the oxidation state of the respective nanoparticles, we reduced the sample within the UHV system by exposure to 1 \( \times \) 10\(^{-6} \) mbar of an H\(_2\)/Ar-atmosphere (25% H\(_2\), 75% Ar) at ~ 675 K for two hours.

Spectroscopic measurements were carried out in an Omicron UHV system, equipped with a DAR400 X-ray radiation source (Al K\( \alpha \) 1486.6 eV) and an AR65 electron analyzer for X-ray photoelectron spectroscopy.
(XPS). Scanning tunnelling microscopy (STM) and spectroscopy (STS) measurements were performed using a variable temperature scanning probe microscope (VT-SPM) within the same UHV system. All STM images were recorded in the constant current mode, using a tungsten tip at a sample bias of -1.5 V and a current of 0.1 nA. The topographic images represent the height \( z(x,y) \) of the tunnelling tip above the sample after a plane and slope subtraction was performed. The STS measurements were carried out placing the tunnelling tip above a single nanoparticle and keeping the tip-sample separation fixed while recording the I(U) characteristic. A Bruker fourier-transform infrared spectrometer (FTIR) was used for optical spectroscopy. STM and STS measurements were done on monolayers of nanoparticles, while XPS and optical spectroscopy measurements were done on thicker samples in order to improve the signal to noise ratio. Such samples were prepared from a small dried drop of Ferritin solution (1 mg/ml) annealed in air at the respective temperatures.

III. RESULTS

Images of monolayers of Ferritin molecules under air (Fig. 1) were taken by Tapping Mode atomic force microscopy (TM-AFM, utilizing a Nanoscope IIIa, Digital Instruments). The layer of Ferritin molecules is not completely closed. The difference in height between the Ferritin layer and the subjacent HOPG substrate of about 10 nm corresponds to the thickness of a single Ferritin monolayer. Also the diameter of the spheres observed is approximately 10 nm, characteristic of Ferritin molecules with a dehydrated protein shell caused by drying under air.

Depending on oxidation parameters, we obtain nanoparticles of different iron oxide phases. X-ray diffraction (XRD) performed on a thick layer of Ferritin annealed at \( \sim 675 \) K under air for one hour (procedure 1) reveals rather broad reflections characteristic of \( \gamma \)-Fe2O3 with some contributions of \( \alpha \)-Fe2O3. In the following we will refer this mixed phase as \( \chi \)-Fe2O3. Further annealing for five hours (procedure 2) resulted in narrow reflections characteristic of \( \alpha \)-Fe2O3. These results are consistent with transmission electron microscopy (TEM) studies, which will be described elsewhere. Annealing Ferritin molecules at \( \sim 575 \) K in air (procedure 3) results in \( \gamma \)-Fe2O3 nanoparticles, as confirmed by TEM.

A STM image of an nanoparticle monolayer after annealing in air (procedure 1) is shown in Figure 2. Here we note that the images of the nanoparticles of all three phases (not shown) look alike. The image shows densely packed clusters of distinguishable nanoparticles. After the annealing process the removal of the protein shell results in a lower coverage of the HOPG surface. The nanoparticle clusters consist of well defined particles of a size of approximately 7 - 8 nm. Such a size is expected for the iron oxide core of Ferritin. Clusters are found dominantly at steps present on the HOPG substrate surface.

To obtain information concerning the iron oxidation state we performed XPS on the nanoparticles. Figure 3 displays the Fe 2p XPS spectra characteristic of the oxidized nanoparticle phases and, for comparison, the spectra of Fe2O3 and FeO, taken from bulk-like material. The latter two spectra correspond to a Fe3+ and a Fe2+ state, respectively. We did not observe any charging effects of the nanoparticles within the instrumental width of about 0.2 eV. With respect to the Fe2+ spectrum, the Fe3+ spectrum is shifted to a higher binding energy by 1.5 eV and shows a characteristic satellite structure at a
binding energy $E_b = 719$ eV. The Fe$^{2+}$ spectrum shows a satellite structure at $E_b = 716$ eV. A Fe 2p$_{3/2}$ peak at 711.7 eV and a satellite structure at about 719 eV in the spectrum taken from the iron oxide nanoparticles is characteristic for a Fe$^{3+}$-state, although the presence of a slight weight of Fe$^{2+}$ can not be ruled out. Further oxidation of the particles within the UHV system at an oxygen partial pressure of $1 \times 10^{-6}$ mbar and a temperature of $\sim 675$ K does not result in changes of the intensity of the characteristic satellite, nor did it shift the spectrum to higher binding energies. We, therefore, conclude that either i. the Fe- atoms of the nanoparticles are already in the highest oxidation state (Fe$_2$O$_3$), or ii. the Fe- atoms are not in the highest oxidation state, but further oxidation of the nanoparticles is not possible under the chosen conditions.

To investigate the electronic excitation spectrum of single nanoparticles in the vicinity of the Fermi energy $E_F$, STS measurements were performed on the three different phases identified by XRD and TEM ($\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$, $\chi$-Fe$_2$O$_3$). It is well known, that tunnelling spectra obtained from nanocrystals may depend on the tunnelling parameters and tunnelling configuration due to e.g. charging\textsuperscript{17,18}, rendering the determined gap width unreliable. Therefore we adjusted the tunnelling parameters to perform the measurements at large tunnelling tip-nanoparticle distance. The distance was increased until a constant gap value was observed and charging effects did not occur.

A typical tunnelling spectrum taken from a single $\alpha$-Fe$_2$O$_3$ nanoparticle (NP) is plotted in Figure 4 for comparison, a spectrum taken from the HOPG substrate is also shown. The $I(U)$ - curves taken from the nanoparticle clearly are characteristic for a gap energy of $\Delta = 2.0$ eV. The variation of the gap energy for spectra taken from the same nanoparticle was within the error of the measurement. Spectra were taken from of a few ten different nanoparticles and the gap energy was found to vary between 1.8 eV and 2.2 eV. This variation might reflect differences in particle size, surface conditions and small variations of the tunnelling junction parameters for the different measurements. The gap energy of $\Delta = 2.0$ eV corresponds to that measured on a bulk $\alpha$-Fe$_2$O$_3$ sample ($\Delta = 2.2$ eV). Figure 5 displays tunnelling spectra taken off $\gamma$-Fe$_2$O$_3$ nanoparticles. Here, spectra taken from different locations of a single nanoparticle, show two different values of the gap energies, $\Delta_1 = 1.3$ eV ($\pm 0.2$ eV) and $\Delta_2 = 2.0$ eV ($\pm 0.2$ eV). We note, that the gap energy of a bulk sample of $\gamma$-Fe$_2$O$_3$ shows a gap of 2.0 eV. Finally, tunnelling spectra taken from $\chi$-Fe$_2$O$_3$ phase nanoparticles show a band gap of 1.3 eV ($\pm 0.2$ eV) (Fig. 6), which does not change for different locations on one nanoparticle. A gap value of 1.3 eV does not correspond to the gap energy of any bulk iron oxide phase\textsuperscript{7}.

Keeping in mind that STS is a highly surface sensi-
tive technique we carried out optical spectroscopy on nanoparticles of the $\chi$-Fe$_2$O$_3$ phase, in order to obtain information corresponding to "bulk properties". Figure 7 shows the optical transmission data taken from a thick layer of such particles. The spectrum displays a strong decrease of transmission at around 2.0 eV, and a less pronounced decrease at about 1.3 eV. These energies agree well with the two different gap energies inferred from STS measurements on such particles. In a straightforward interpretation we assign the feature at 2 eV to the bulk gap, the feature at 1.3 eV to a surface gap. This interpretation will be discussed in more detail below.

An interesting question concerns the possibility to manipulate the electronic properties of the nanoparticles. To this end we exposed $\chi$-Fe$_2$O$_3$ nanoparticles in situ at a temperature of $\sim$ 675 K to a reducing H$_2$/Ar atmosphere of $1 \times 10^{-6}$ mbar (25% H$_2$, 75% Ar) for two hours. Figure 8 compares the Fe 2p spectrum of the nanoparticles before and after reduction. As is clearly seen, the spectrum of the reduced sample is shifted to lower binding energies by about 1.2 eV compared to the spectrum before reduction. In addition, a Fe$^{2+}$ satellite structure develops, marked by an arrow in Figure 8.

STM imaging shows (Figure 9) that shape and size of the nanoparticles are not changed by the reduction process. From STS measurements we infer, within the margins of error, the same gap of 1.3 eV ($\pm$ 0.2 eV) as before the reduction (Figure 10).

IV. DISCUSSION

We first address the question of the valence of the iron ions in the nanoparticles. From the Fe 2p binding en-
energy and the position and intensity of the corresponding satellite structure as measured by XPS we conclude that the iron valence state of the oxidized samples is Fe$^{3+}$. This is in agreement with expectations since it is well known that ferrihydrites transform into α- or γ-Fe$_2$O$_3$ at 573 - 723 K under air. Further evidence for an Fe$^{3+}$-state after annealing under air comes from XRD and TEM, which show the nanoparticles to consist of different phases of Fe$_2$O$_3$, depending on the oxidation procedure. Bulk Fe$_2$O$_3$ is an insulator with a gap of $\Delta = 2.0$ eV for the γ-phase and $\Delta = 2.2$ eV for the α-phase. The gap energy obtained for α-phase nanoparticles by STS is consistent with that for bulk material. The γ-Fe$_2$O$_3$ phase nanoparticles show a band gap of 1.3 eV or 2.0 eV, depending on the location of the tunnelling tip on the same particle. This suggests two different types of phases within one nanoparticle. The fact that bulk γ-Fe$_2$O$_3$ has a band gap of 2.0 eV suggests that it is one of these phases. From single crystal studies it is known that γ-Fe$_2$O$_3$ crystallizes in an iron deficient structure similar to the inverse spinel structure of Fe$_3$O$_4$ (A[BA]O$_4$, A=Fe$^{3+}$, B=Fe$^{2+}$), but in γ-Fe$_2$O$_3$ there are randomly distributed cation vacancies on the B-site. Such a defect rich structure might be subject to reconstruction effects, especially at the surface of a nanoparticle or by impurity atoms like, e.g. carbon introduced by the original organic shell of the particle. Such a reconstructed phase can yield a different gap than the bulk. The XPS and FTIR measurements might be affected by such surface effects in a much lesser degree because of their lower surface sensitivity. This will be discussed in more detail below.

The FTIR-spectrum taken from the χ-Fe$_2$O$_3$ phase sheds further light on the origin of the 1.3 eV gap. Two significant features were identified in this spectrum, one of which coincides with the gap of 1.3 eV found by STS. From the fact that the slope of the absorption coefficient is much smaller at 1.3 eV than at 2 eV, but that the surface sensitive STS measurements detect only one gap at 1.3 eV we conclude that the 1.3 eV gap is a property of the surface of the nanoparticle, most likely due to a surface reconstruction. The bulk of the nanoparticle then exhibits the gap expected from bulk γ- or α-Fe$_2$O$_3$. It is striking that a surface reconstruction would only occur in the γ-Fe$_2$O$_3$ and χ-Fe$_2$O$_3$ nanoparticles. The reason for this could be attributed to the defect rich nature of these phases.

The interpretation of the 1.3 eV gap as a surface effect is further corroborated by our reduction experiments. There are several studies concerning the reduction of iron oxides. For example, α-Fe$_2$O$_3$ can be reduced to metallic iron via a series of intermediate oxides, like Fe$_3$O$_4$ and FeO. As shown above we achieved a significant reduction of χ-Fe$_2$O$_3$ nanoparticles by annealing in H$_2$/Ar atmosphere, as evidenced by XPS measurements. The resulting XPS spectrum is compatible to a FeO reference spectrum taken from a macroscopic sample. However, a stable cation-deficient phase of FeO exists at ambient pressure only at temperatures above 840 K. This non-stoichiometric form of FeO can be obtained as a metastable phase at room temperature by rapid quenching. Although we cannot expect a stable FeO bulk phase from the applied annealing procedure under ambient conditions, we cannot exclude that the FeO phase is stabilized under UHV due to its nanocrystalline form. This conclusion is supported by former studies on epitaxial films showing that the stabilization of a FeO phase depends on film thickness.

Interestingly, a change of the iron oxidation state under reducing conditions, as reflected in the XPS measurements, does not affect the energy gap of the nanoparticles as measured by STS. Taking into account the probing depth of XPS at the Fe 2p binding energy we conclude that about 40 % of the volume of a particle contributes to the XPS spectrum, while contributions to the STS measurements originate from a surface layer of the particle, which amounts to only 10 % of its volume. Obviously, for nanoparticles XPS is far more bulk sensitive than STS. Therefore, we attribute the independence of the gap value upon iron reduction to the fact that the gap value measured by STS is dominated by the surface structure of the nanoparticle. This surface structure appears to be unaffected by reduction. This finding is consistent with our the conclusion above that the 1.3 eV band gap of χ-Fe$_2$O$_3$ is due to surface effects.

In conclusion, only nanoparticles of the thermodynamically stable α-Fe$_2$O$_3$ phase show a band gap compatible to the bulk material in surface sensitive STS measurements. The STS measurements on all other nanoparticle phases investigated (γ-Fe$_2$O$_3$, χ-Fe$_2$O$_3$ and FeO) demonstrate the existence of a surface band gap of 1.3 eV, although volume sensitive measurements reveal a band gap compatible with the bulk material. We, therefore, conclude that the band gap does not depend on the size of the nanoparticles for diameters above 8 nm, but that properties, like e.g. the photocatalytic activity of such...
particles, are due to the formation of a surface band gap different from that of the volume. The existence of such a surface band gap appears to be triggered by defects within the nanoparticle.

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