Zinc Oxide Nanoparticles with Defects**

By Vladislav Ischenko, Sebastian Polatz,* Dirk Grote, Victorina Stavarache, Karin Fink, and Matthias Driess*

Dedicated to R. Knip on the occasion of his 60th birthday

Zinc oxide in the form of nanoscale materials can be regarded as one of the most important semiconductor oxides at present. However, the question of how chemical defects influence the properties of nanoscale zinc oxide materials has seldom been addressed. In this paper, we report on the introduction of defects into nanoscale ZnO, their comprehensive analysis using a combination of techniques (powder X-ray diffraction (PXRD), X-ray absorption spectroscopy/extended X-ray absorption fine structure (XAS/EXAFS), electron paramagnetic resonance (EPR), magic-angle spinning nuclear magnetic resonance (MAS-NMR), Fourier-transform infrared (FTIR), UV-vis, and photoluminescence (PL) spectroscopies coupled with ab-initio calculations), and the investigation of correlations between the different types of defects. It is seen that defect-rich zinc oxide can be obtained under kinetically controlled conditions of ZnO formation. This is realized by the thermolysis of molecular, organometallic precursors in which ZnO is pre-organized on a molecular scale. It is seen that these precursors form ZnO at low temperatures far from thermodynamic equilibrium. The resulting nanocrystalline ZnO is rich in defects. Depending on conditions, ZnO of high microstructural strain, high content of oxygen vacancies, and particular content of heteroatom impurities can be obtained. It is shown how the mentioned defects influence the electronic properties of the semiconductor nanoparticles.

1. Introduction

The reason for the “nano-hype” that, recently, has conquered all disciplines of natural sciences is the observation that properties of materials depend not only on composition but also on morphology (size and shape). For materials with at least one dimension below 50 nm, the contribution of surface energy to total energy becomes more and more significant the smaller the structures get. Just as chemical and physical properties of surfaces differ from those of the bulk, so do those of nanoscale materials. For (semi)conductors, as the particles become smaller an additional effect, the so-called quantum-size effect, influences, in particular, the bandgap size, and consequently the electronic properties of the material.[1–4] Therefore, particular attention has been devoted to the preparation of nanoscale semiconducting materials.[5] Among these, nanoscaled ZnO is of extraordinary importance and a substantial number of papers have been published reporting on ZnO nanostructures.[5]

The application of ZnO ranges from catalysis via gas sensing to UV-light emitters, ceramic varistors, transparent high-power electronics, surface acoustic wave devices, and piezoelectric transducers.[6] Of particular interest is also the use of ZnO as a component of composite catalysts,[7–9] for instance for low-pressure methanol synthesis.[10,11] Existing models of methanol synthesis on the ZnO surface and recent theoretical calculations suggest that oxygen vacancies formed on the surface of ZnO crystals may be the active sites for CO (and CO2) chemisorption when methanol synthesis is initiated.[12–15]

This points to an interesting issue: (some) key properties of ZnO may depend not only on intrinsic properties such as the particular crystal structure, bulk composition, and morphology of the oxide particles, but furthermore on their defect structure as well.

Thus, it is becoming increasingly established that in order to control the functional properties of nanoscale materials it is necessary to control not only their composition and morphology but also their defect structure.[16–19] To understand and ultimately to control the defect content of inorganic nanostructures can be seen as an important goal.

As already indicated for heterogeneous catalysis, oxygen defects are of particular importance in the case of zinc oxide, leading to deviations in the zinc-to-oxygen ratio (ZnO,9999) at 800 °C.[20] “Empty” oxygen sites (oxygen vacancies, VO2+) are potential wells that can trap either one (VO+) or two (VO2+) electrons.[21–26] In addition, the occurrence of interstitial zinc atoms is known. The latter are shallow donors while oxygen vacancies create deep levels.