

XAFS STUDY OF Mo AND W DOPED TiO₂ NANOPOWDERS

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The solar light-assisted generation of hydrogen from water using semiconductor electrode has attracted a growing interest in the search for new environment-friendly energy sources [1]. In recent years, the main photo-electrode candidate has been established to be TiO₂ [2]. A disadvantage of TiO₂ in the application as the photo-electrode is a poor absorption of visible light due to its wide energy gap (ca 3.2 eV) and losses in recombination processes of the photo-charge pairs. Several techniques for improving the photo-response of TiO₂ towards visible range have been proposed. Among them the most promising appears to be doping by other transition metals like W and Mo into TiO₂ crystal lattice. The aim of this work is the study of the incorporation mechanism of these elements into the TiO₂ crystal lattice and their impact on the local structure of nanocrystalline TiO₂ by means of X-ray absorption fine structure (XAFS) spectroscopy.

Nanoparticle materials of WO_x-TiO₂ have been synthesized by Flame Spray Synthesis (FSS) process by oxidation of metal-organics precursors [3]. Titanium tetraisopropoxide (TTIP) and tungsten hexacarbonyl (THC) dissolved in tetrahydrofuran (THF) were used as a precursor sources of TiO₂ and WO₃, respectively. Concentration of W (0.1 - 1 at%) has been varied by changing experimental parameters like flow rate or concentration of precursors. Particle size, phase composition and morphology of the nanopowders were studied using BET, X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively.

XAFS experiments have been carried out in the synchrotron laboratory HASYLAB/DESY, Hamburg. The measurements at the K edge of titanium were done at the experimental station E4 at room temperature in transmission mode. The main peak located at about 1.7 Å, which corresponds to oxygen neighbours to a titanium ion reveals a decrease with increasing doping level. The effect can be attributed to the increasing amount of oxygen vacancies in the next neighbour shell to the Ti ions. The peak at about 3.4 Å which corresponds to Ti neighbours also decreases its intensity with increasing doping, which possibly indicates an

increased amount of Ti vacancies. The 0.5% Mo doped sample is an exception with a similar amount of Ti vacancies as in the pristine TiO₂.

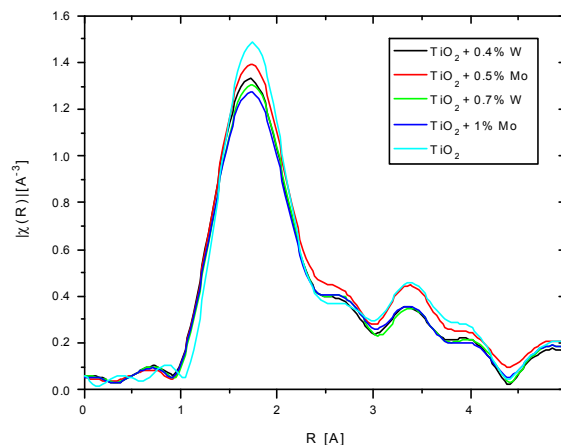


Figure 1. Fourier transforms of the Ti:K edge EXAFS functions.

The Ti:K edge XAFS study of the TiO₂-based nanomaterials indicates an increased amount of oxygen and titanium vacancies on doping with an exception for low Mo doping which creates oxygen vacancies only. The results are compared to the Mo:K edge and W:L edges XAFS and the X-ray diffraction data.

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