X-ray Absorption Studies of Titanium Dioxide Nanoparticles, Nanorods, and Nanosheets

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Introduction

Semiconductor TiO_2 nanoparticles have been extensively studied because photoirradiation with photon energies larger than the bandgap (3.2 eV) creates electron-hole (e-/h+) pairs that act as either electron or donors hole donors to reduce or oxidize materials in the surrounding media. During the past several years, we have been investigating the structural origins of new chemical properties that appear in nanostructures and are brought about by surface modification. We identified the surface defect sites with spectral evolution as a function of the nanoparticle size, since spectral features responsible for the defects increase with shrinkage of the particle. Recently, TiO_2 nanostructures with different shapes such as cubes, tubes, and sheets were synthesized, which has brought about the possibility of controlling TiO_2 properties in photochemical reactions.

Methods, Materials, and Results

Following our previous pursuit, we used x-ray absorption spectroscopy (XAS) to investigate the structural origins of the chemical properties of other TiO_2 nanostructures. Although TiO_2 nanoparticles have the lattice structure of anatase, TiO_2 nanosheets have the rutile structure indicated by their x-ray absorption near-edge structure (XANES) features (Fig.1) and by peaks in the Fourier transform x-ray absorption fine structure (XAFS) spectra that coincide with rutile peaks (Fig. 2). However, the much-enhanced pre-edge peaks and smoothed XAFS features in the freshly made sheets suggest local disorder, which is confirmed by their evolution to those features in bulk rutile as the sheets age. The tubes have a more ordered, anatase-like structure, with severe distortion from the regular anatase lattice. It is remarkable that by controlling the pH in the solution, the nanotubes with anatase-like structure can be opened up to sheets with a rutile-like lattice. Our studies revealed how nanostructure could change the condition for the phase transition in TiO_2. Moreover, the nanocubes, synthesized by hydrothermal methods, have an ordered anatase lattice structure, in contrast with nanoparticles of similar dimension.

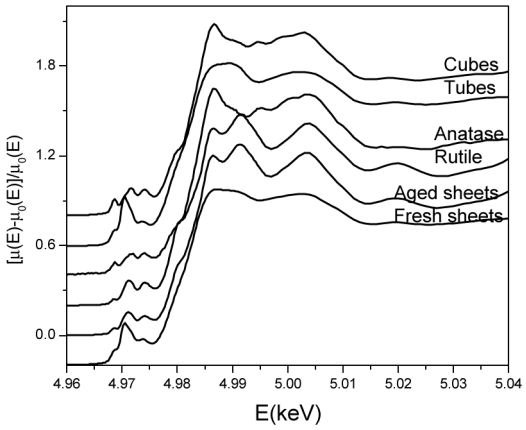

FIG. 1. XANES spectra of nanastructured TiO_2 with difference shapes.

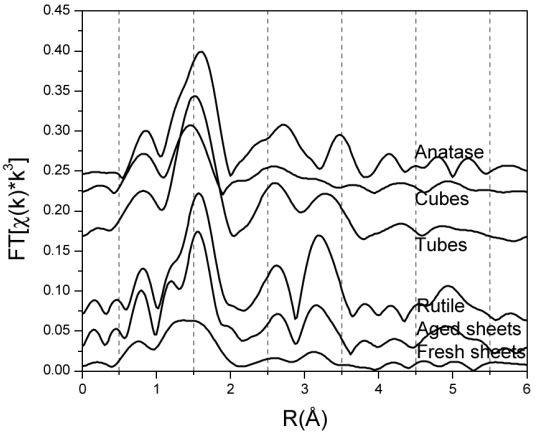

FIG. 2. FT-XAFS spectra of nanostructured TiO_2 with different shapes.

Discussion

XAFS and XANES have proven to be useful tools for identifying local structural disorder for different nanostructured TiO_2 materials. The structural information combined with the results of photochemical studies can be used to reveal the structure-function relationship and design particular nanostructures for targeted functions.

Acknowledgments

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