Nanoscale NEXAFS analysis of individual N-doped TiO$_2$ nanoribbons

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Abstract
Nitrogen doping titanium dioxide (TiO$_2$), with N at substitutional sites has been reported to be indispensable for enhancing the use of TiO2 as a visible-light photocatalytic material. The main effect of the N-doping is the narrowing of the energy band gap of TiO$_2$ due to the mixing of N 2p and O 2p states. Additionally, an isolated narrow band responsible for the visible light photoactivity is formed above the valence band. Nitrogen doping into the TiO$_2$ lattice is rather challenging as N atoms must be accommodated geometrically and electronically. To address the fundamental issues we explored a chemical route and report here a comprehensive investigation of N-doped TiO$_2$ nanoribbons. As a precursor material for N-doped TiO$_2$ nanoribbons we used hydrogen titanate nanoribbons (HTiNRs) because upon heating HTiNRs easily transform first to the monoclinic TiO$_2$ β-phase (TiO$_2$-B) and then to anatase (tetragonal phase) while retaining the morphology of the parent nanostructure intact.

The nitrogen doping of TiO$_2$ nanoribbons during the thermal transformation of hydrogen titanate nanoribbons (HTiNRs) between 400 and 800 °C in a dynamic ammonia atmosphere was investigated using X-ray photoelectron spectroscopy (XPS) and transmission X-ray microscopy combined with near-edge X-ray absorption fine structure spectroscopy (NEXAFS-TXM). XPS results clearly reveal the nitrogen doping of TiO$_2$ nanoribbons and that, depending on the calcination temperature, nitrogen atoms occupy interstitial and substitutional sites. Moreover, in samples calcined at 580 and 650 °C the presence of N$_2$-like species in the HTiNRs was detected by NEXAFS-TXM. These species are trapped in the HTiNRs structure.