Orientation effects in morphology and electronic properties of anatase TiO_2 one-dimensional nanostructures. I. Nanowires

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Phys. Chem. Chem. Phys., 2014,**16**, 9479-9489

DOI: 10.1039/C3CP54988G

Received 26 Nov 2013, Accepted 26 Mar 2014

First published online 26 Mar 2014

Abstract

By means of *ab initio* calculations we have revealed the existence of sizable anisotropy in electronic properties of anatase TiO_2 nanowires with respect to orientation: nanowires with 〈001〉, 〈100〉 and 〈110〉 axes are found to be direct band-gap, indirect band-gap and degenerate semiconductor materials, respectively. The degenerate semiconducting properties of 〈110〉-oriented TiO_2 nanowires are predicted to be the intrinsic features closely connected with stoichiometry. A band-gap variation with nanowire diameter is also shown to display rather complex behavior characterized by a competition between quantum confinement and surface state effects that is fully compatible with the available contradictory experimental data. Finally, we propose a model to explain the band-gap variation with size in TiO_2 nanowires, nanocrystals and thin films.