Orientation effects in structural and electronic properties of anatase TiO_2 nanowires and nanotubes

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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 an intrinsic feature closely connected with stoichiometry. It is also shown a band-gap variation with nanowire diameter to display rather complex behavior characterized by a competition between quantum confinement and surface states effects that is fully compatible with available contradictory experimental data. Finally, a model to explain the band-gap variation with size in TiO_2 nanowires, nanocrystals and thin films is proposed. In addition, we present results indicating crucial changes in morphology of anatase TiO_2 nanotubes originated from TiO_2 nanowires by making a hole along the wire axis. The critical wall thickness has been found to exist for the nanotubes with <001> and <110> axes: at smaller thickness their shape can be rounded, squeezed, viewed as conglomerates of nanocrystals and even represented as cylindrical and 'single-walled'-like structures formed without rolling up a thin titania layer into a nanotube. In general, band dispersion near the gap region of TiO_2 nanotubes are close to the one of TiO_2 nanowires with the same orientation. We have also revealed that optimization of the unit cell parameter along the wire axis and consideration of quantum confinement and surface states effects are important to provide an interpretation of band-gap variation with respect to wall thickness in TiO_2 nanotubes.