

The oxidation state of titanium in titanium dioxide is +3, not +4

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Titanium dioxide (TiO₂) is a material widely used in numerous technologies. TiO₂ polymorphs are large-band-gap semiconductors which makes them suitable for applications in photocatalysis and solar cells and as electrode materials for Li-ion and Na-ion batteries, due to their potentially high capacity, cycling stability and charge/discharge rate. The band structure of titania compounds was reported extensively, commonly describing the valence band as being primarily composed of O 2*p* states and the conduction band mostly consisting of Ti 3*d* contributions. At the same time, the density of states shows other less important contributions, notably from Ti 3*d* states in the valence band.

The oxidation state of titanium in titanium dioxide is commonly assumed to be +4. This assumption is used ubiquitously to rationalize phenomena observed with TiO₂ in all the above applications; for example the assignment of oxidation states obtained in doped TiO₂ is done off the assumed +4 oxidation state in pure TiO₂. This assumption is based on qualitative MO considerations. Indeed, the often-cited basis for the assumption of Ti⁴⁺, photoelectron spectroscopy, relied on these very considerations to interpret XPS peaks. There does not seem to be direct, independent experimental evidence of the absolute oxidation state.

We present a comprehensive electronic structure investigation of Ti ions, TiO₂ molecules and TiO₂ bulk crystals, using different density functional theory and wave function-based approaches, which suggests a lower oxidation state. Specifically, there is evidence of a significant remaining contribution from valence *s* and *d* electrons of Ti, including the presence of a nuclear cusp around the Ti core. The charge corresponding to valence *s* and *d* states of Ti amounts to 1*e* and cannot be assigned to any other atom than Ti. The oxidation state of Ti in TiO₂ is therefore +3. The respective oxidation state of oxygen would therefore correspond to -1.5. Our results suggest that, in principle, further oxidation at the Ti centers is possible. Conversely it follows that oxygen could be further reduced; indeed, oxygen redox activity is a known effect occurring e.g. upon Li intercalation in several cathode materials.

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