How do anatase and rutile differ in their photocatalytic activity?

Titanium dioxide is generically a photocatalytic material among the semiconductor metal oxides due the dissimilar nature of the valence and the conduction bands. This increases the life of the electron-hole pair generated by the incident near UV radiation. These holes and the electrons initiate the redox reactions in the adsorbate.

Both the anatase and the rutile have a tetragonal crystal structure with the anatase unit cell having higher volume compared to the rutile. The anatase form possesses a band gap of 3.2 eV with the absorption edge at 386 nm which lies in the near UV range. The rutile form has a lower band gap of 3.02 eV with the absorption edge in the visible range at 416 nm.

While both the crystal forms possess significant photocatalytic activity, the anatase form has been found to exhibit higher activity compared to the rutile. The mechanism responsible for this behavior is a controversial subject. Considerable research is in progress to gain complete understanding into this phenomenon. However, at present there are four hypotheses seeking to explain higher photocatalytic activity of anatase:

- Crystal size, surface area, defect population and porosity: These factors influence the rate of recombination of the holes and the electrons. Any generic difference in these aspects between rutile and anatase can lead to a significant difference in their photocatalytic activity.
- Higher Fermi level: The anatase has higher Fermi level over the rutile by 0.1 eV. This leads to a lower oxygen affinity and a higher level of hydroxyl groups on the surface. These hydroxyl groups contribute to the higher photocatalytic activity.
- Indirect band gap: The anatase possesses an indirect band gap while the rutile has a direct band gap. In a direct band gap material, the minimum in the conduction band coincides with the maximum in the valence band, thus facilitating an early return of the electron to the valence band. In the indirect band gap materials, the minimum in the conduction band is away from the maximum in the valence band. This enables the excited electron to stabilize at the lower level in the conduction band itself leading to its longer life and greater mobility.

- Excitation electron mass: Anatase possesses wider absorption gap. Hence, it is proposed that excitation electron mass of the outer shell electrons in the anatase may be lower than in the case of the rutile. This may explain higher mobility of electrons in the anatase.

In practical terms, both the crystal forms have been found to be photocatalytic to different degrees. In some cases, the combination of anatase and rutile in 70:30 ratio is found to display the highest activity. Here, the higher absorption of visible light by the rutile is supposed to synergistically enhance the activity of anatase.
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