Why do only certain semiconductor metal oxides like TiO2 and ZnO behave as photocatalysts?

For a material to function as a photocatalyst, it must satisfy the following criteria:

1. It must possess an electron band gap corresponding to the wavelengths in ambient radiation (near UV/ visible) so as to cause absorption of the photons. This will lead to the excitation of the electrons from the valence band to the conduction band.
2. The excited electrons should remain separated from the positively charged valence band (containing holes) long enough for them to react with the adsorbed species to initiate a chemical reaction. This is enabled by preventing immediate recombination of the electrons with the holes.

Most of the semiconductor metal oxides will meet the first criterion, but only TiO2 and ZnO meet the second one. Let us see why this happens.

TiO2: The atomic number of titanium is 22 and its electronic configuration is: ***1s2, 2s2, 2p6, 3s2, 3p6, 3d2, 4s2.***Thus the outer shell electrons are in the 3*d* & 4*s* orbitals. The atomic number of oxygen is 8 and its electronic configuration is: ***1s2, 2s2, 2p4.*** Thus the outer shell electrons are in 2s and 2p orbitals.

In titanium dioxide, the highest occupied molecular orbital (HOMO) in the valence band is formed by the hybridization of 3*d* orbitals of titanium and 2*p* orbitals of oxygen. The conduction band or the lowest occupied molecular orbital (LUMO) is made up of only pure 3*d* orbitals of titanium. This gives rise to a difference in the nature of the HOMO and LUMO ('dissimilar parity') which retards the return of the excited electron in the pure *d* state to the valence band. The electron thus retains its excited state longer, which in turn triggers the reaction with the adsorbate.

ZnO: The atomic number of zinc is 30 and its electronic configuration is: ***1s2, 2s2, 2p6, 3s2, 3p6, 3d10, 4s2.*** Thus the outer shell electrons are in the 3*d* & 4*s* orbitals. The *d* orbitals are completely filled up. The outer shell electrons in oxygen are in 2*s* and 2*p* orbitals.

In zinc oxide, the highest occupied molecular orbital (HOMO) in the valence band is made up of *d* orbitals. The conduction band or the lowest occupied molecular orbital (LUMO) is formed by of only *s p*

hybridized orbitals. This again gives rise to a difference in the nature of the HOMO and LUMO ('dissimilar parity') which retards the return of the excited electron to the valence band. The electron thus retains its excited state longer which in turn initiates its reaction with the adsorbate.

For all the other 3*d* transition metal oxides, the nature of HOMO and LUMO is similar (3d type 'similar parity') and hence there is an immediate return of the electron to the valence band leaving no time for chemical reaction of the electron with the adsorbate. Hence TiO2 and ZnO are special materials as far as photocatalytic activity is concerned. The reduction of the particle size to nanoscale further enhances the catalytic activity due to elimination of crystal defects and generation of larger surface area.
(Ref: 'Physics and chemistry of photocatalytic titanium dioxide: Visualization of bactericidal activity using atomic force microscopy': S Bannerji, Muraleedharan, Tyagi, Raj; Current Science, Vol. 90, No.10, 25 May 2006)

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