THE FUTURE OF PHOTON-ASSISTED SEMICONDUCTOR CATALYSIS

DO WE REQUIRED A PARADIGM SHIFT?

REVISIT 1

ON BASIC PRINCIPLES

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CONTENT

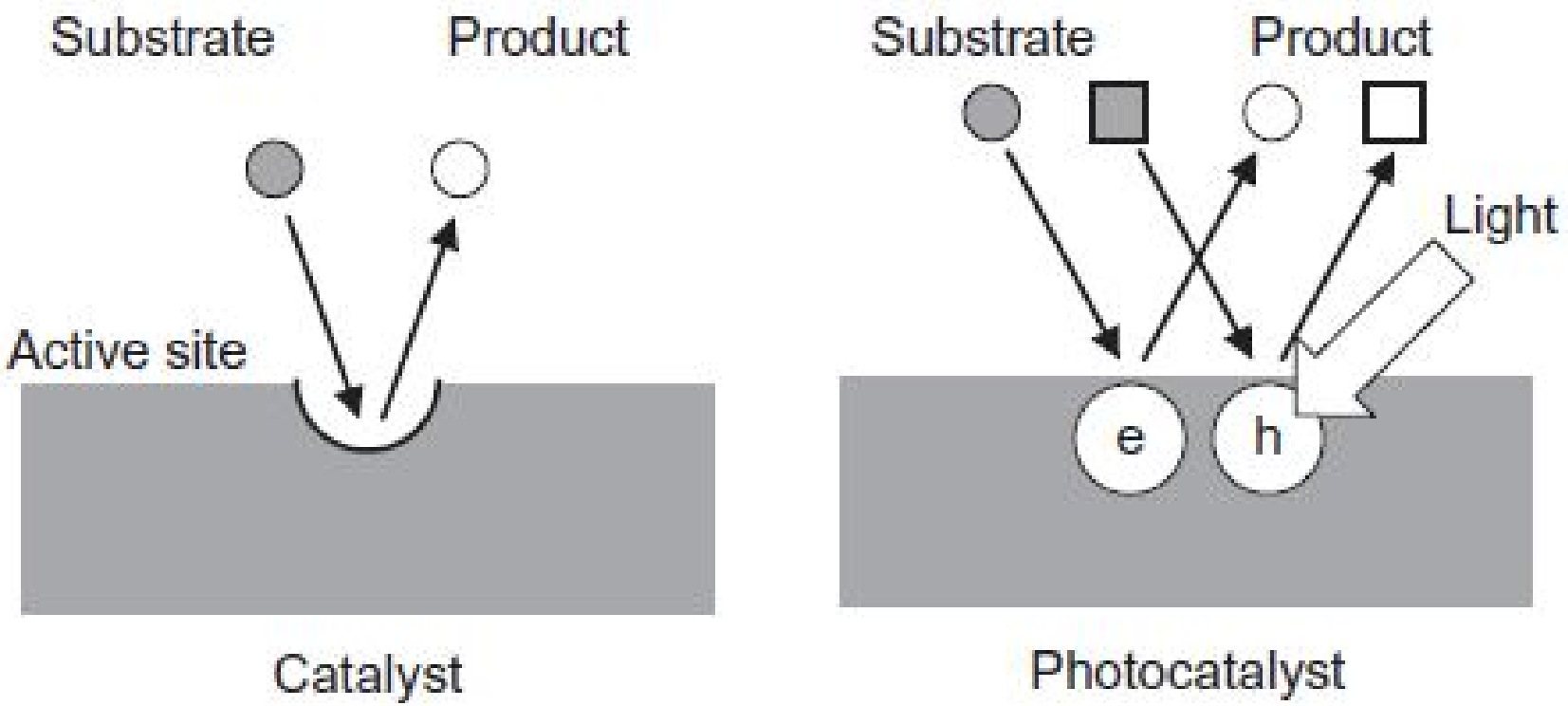
ON PARADIGM SHIFT

1. A paradigm shift, a concept identified by the American physicist and philosopher Thomas Kuhn, is a fundamental change in the basic concepts and experimental practices of a scientific discipline.
2. **A fundamental change in approach or underlying assumptions.**
3. "Geophysical evidence supporting Wegener's theory led to a rapid paradigm shift in the earth sciences"
4. Kuhn, Thomas S. The Structure of Scientific Revolutions. Chicago :University of Chicago Press, 1970. Total Citation : 104204 (Google Scholar)

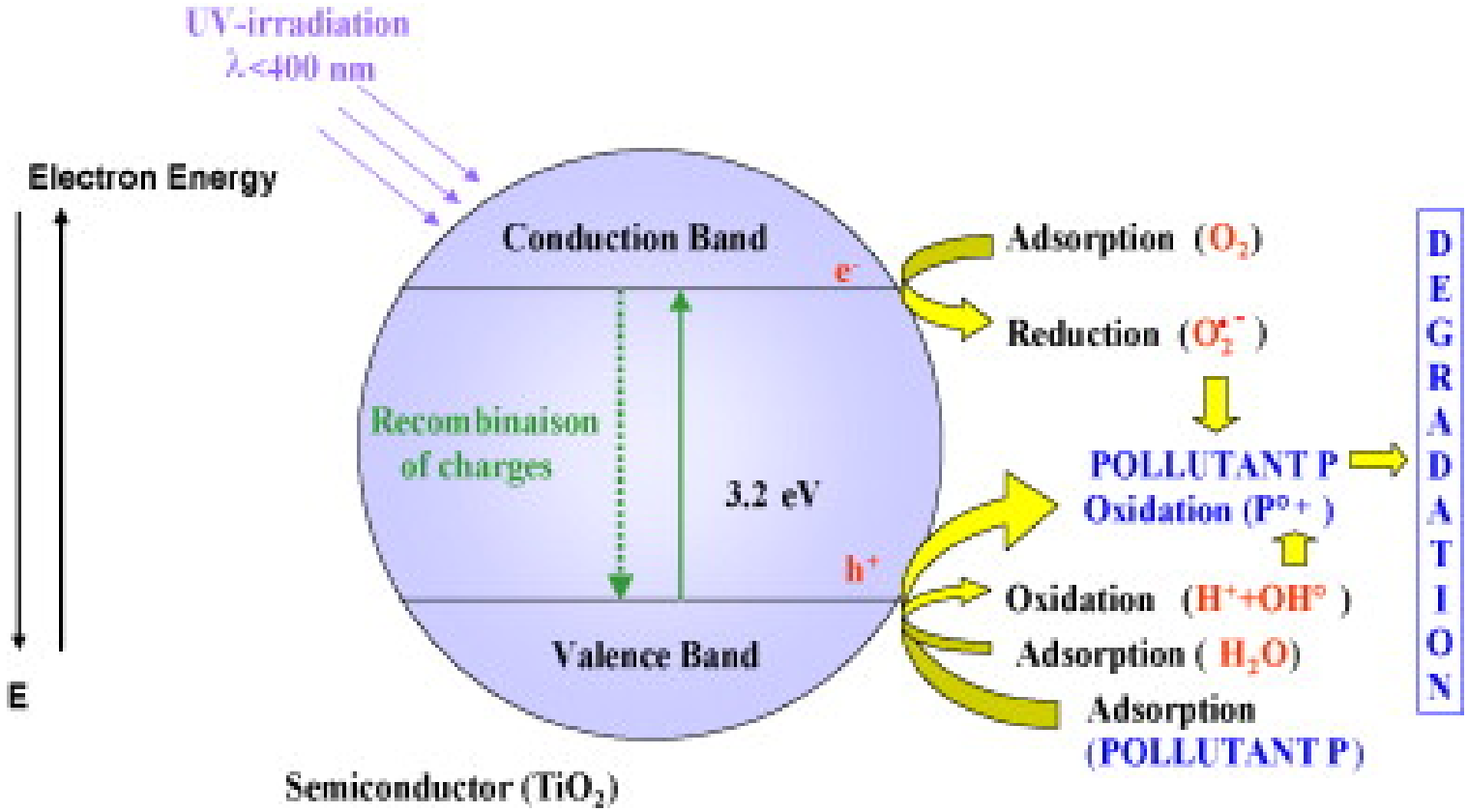
Why This Revisit

1. More than 100 years of history.
2. Nearly 50 years of extensive research in search of a new material
3. Many advances has made yet no materials has been found as a champion.
4. Still we are searching for a materials using a framework which not clear yet.
5. Many of the fundamentals of photon-assisted semiconductor catalysis are not clear yet and we are using the theory evolved for photoelectrochemistry directly to the solid powder/liquid interface.

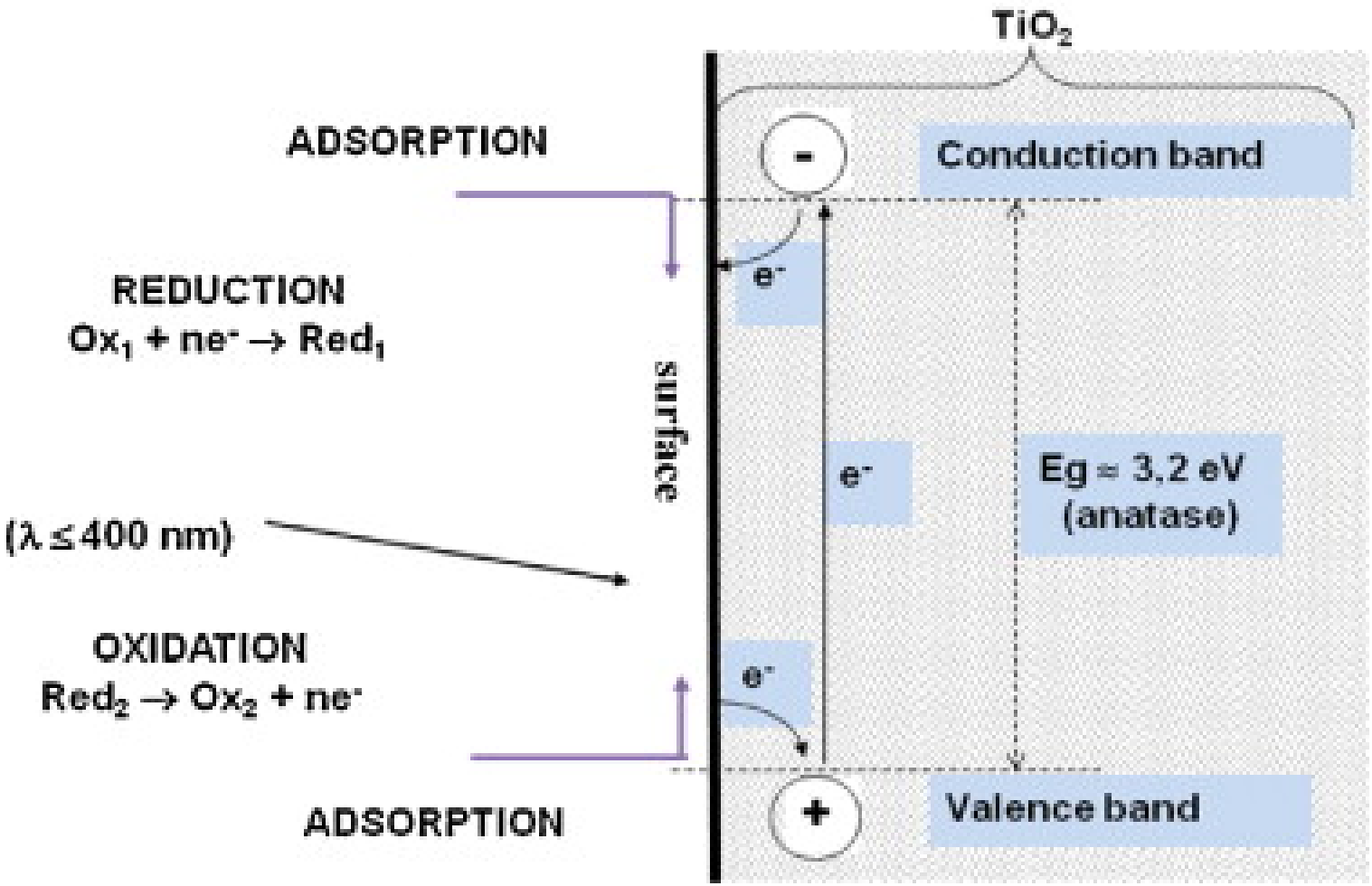
Catalyst, Photocatalyst and Photoactivity



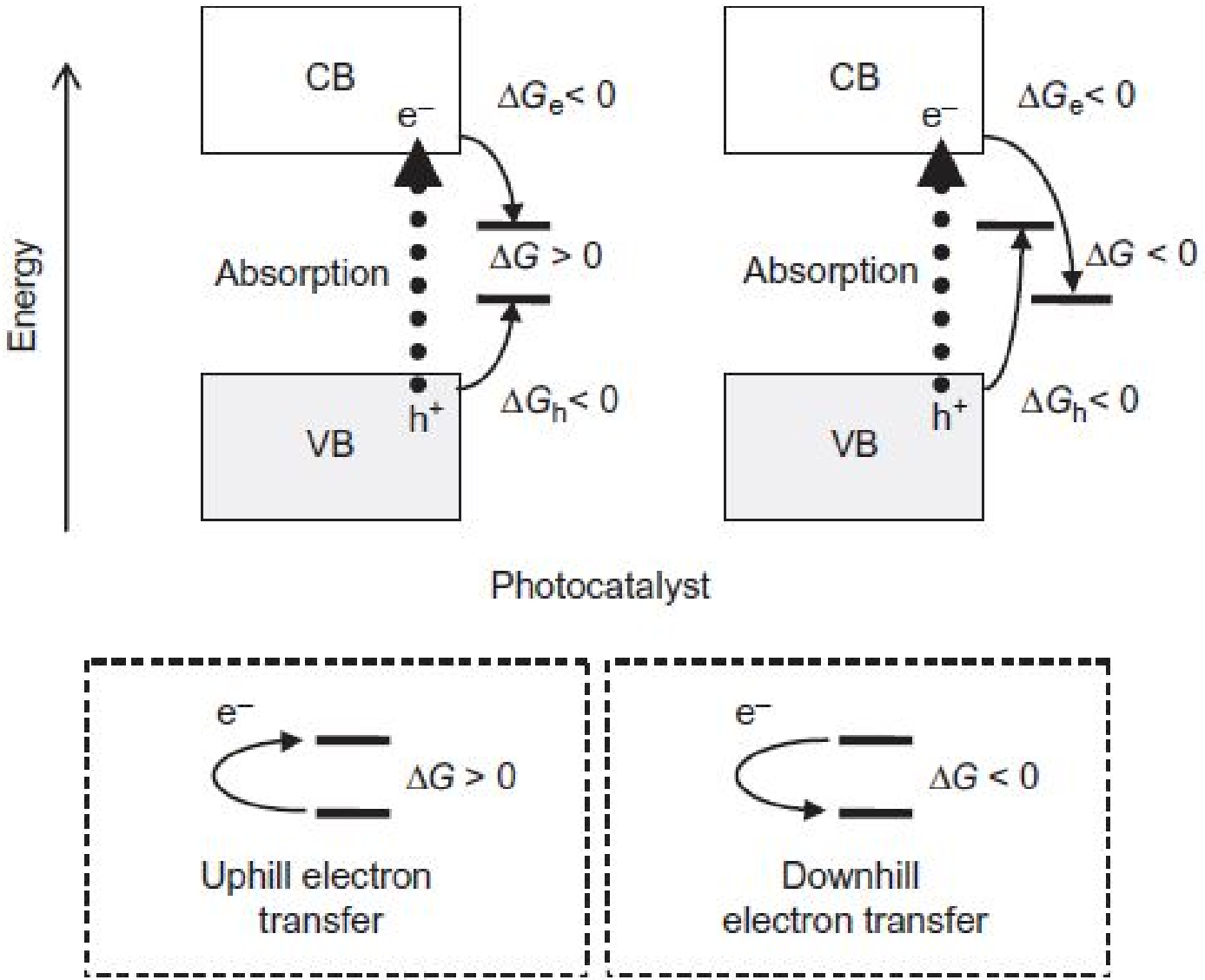
Energy Band Diagram



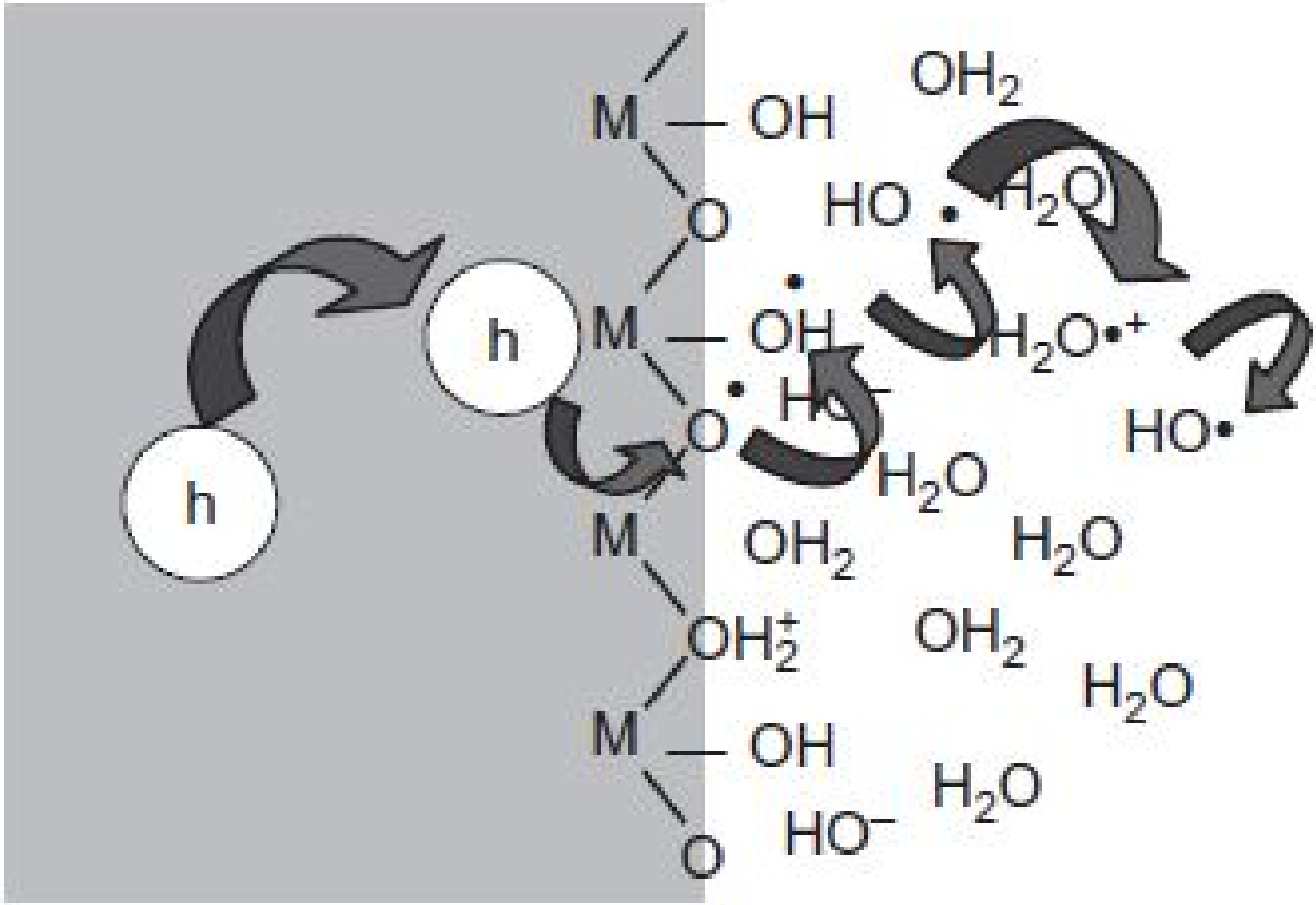
Energy Band Diagram



Energy Band Diagram



Hydroxyl Radicals and Other Active Species



The Recombination

1. Direct recombination of electron and hole via bimolecular pathway.

$$e^- + h^+ \rightarrow h\nu \tag{1}$$

2. The trapping of charge carriers by defects and the carrier recombination that occurs through such defects, that is, recombination centers R, are completely ignored in the photocatalytic landscape.

$$e^-(h^+) + R \rightarrow R^-(R^+) \tag{2}$$

$$R^-(R^+) + h^+(e^-) \rightarrow R \tag{3}$$

3. A single recombination event occurring through the defects is more efficient than the band-to-band recombination of the free charge carriers (reaction 24). The issue here is that band-to-band recombination requires the fulfillment of no less than two important conditions: (1) the conservation of energy, and (2) the conservation of momentum, both of which significantly decrease the efficiency of the band-to-band recombination process.

The Recombination

1. For radiative recombination, the energy conservation law can easily be accounted for by the emission of photons with the corresponding energy. The momentum conservation law given by eq 4 (in which p_e and p_h are the momenta of the recombining photoelectron and photohole, respectively) demands that the algebraic sum of two rather large values (eq 5, in which a is a constant of the crystalline solid) must be very small to be equal to the momentum of the photon (eq 5; ì is the photon wavelength). Because the momentum of the photons p_h is nearly 0 compared to the momentum of free charge carriers, the possibility for recombination through the band-to band pathway is restricted only to those electrons and holes that possess the same momentum.

$$p_e + p_h = p_{ph} \tag{4}$$

$$p_e \approx p_h \approx \frac{h}{2\pi a} \tag{5}$$

The Recombination

1. The recombination of charge carriers through defects in wide band-gap solids (e.g., TiO_2, ZnO, ZrO_2, and others) is a more effective process.
2. The belief that free charge carriers recombine through a bimolecular recombination pathway is yet another misconception in heterogeneous photocatalysis.

Next

1. REVISIT 2 : HISTORICAL NOTES ON PHOTON-ASSISTED SEMICONDUCTOR CATALYSIS
2. REVISIT 3 : DESIGN OF ACTIVE PHOTOCATALYSTS
3. REVISIT 4 : KINETICS
4. REVISIT 5 : LIGHT MATTER INTERACTION
5. REVISIT 6 : DEFECT PROCESSES IN SEMICONDUCTOR
6. REVISIT 7 : PHOTOCATALYTIC CHARACTERIZATION

ANY QUESTIONS?