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# $TiO_2$-MgO mixed oxide nanomaterials for solar energy conversion

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ABSTRACT

Mixed oxide materials have been intensely investigated in catalysis. In recent years, photoactive species have been deposited on high surface area supports and investigated for a variety of applications that include Dye Sensitized Solar Cells (DSSC), photocatalytic and photoelectrochemical splitting of water, and photocatalytic degradation of organics. Basic materials like MgO are attractive as supports for the above mentioned applications, since they can be synthesized conveniently with relatively large surface areas and porosities. The wide band gap (>7 eV) and hence the insulating nature of MgO also lends itself to interesting uses in several applications involving solar energy conversion. The presence of low amounts of MgO has been found to be beneficial for DSSC, photo-electrochemical splitting of water, and photocatalytic degradation of dye molecules and will be discussed in-depth in this review.



## 1. Introduction

### 1.1. Solar energy conversion and photocatalysis

Solar hydrogen is an attractive solution to the impending energy crisis since it is renewable, clean with no production of greenhouse gas emissions, potentially inexpensive, and sustainable. Producing chemical energy, as opposed to electrical energy, has its own advantages such as prolonged storage of energy and easy transport. Even though hydrogen produced from solar energy conversion by either photocatalytic or photoelectrochemical methods is promising, there are enormous challenges in deploying this on a practical scale, owing to lack of materials that are robust, capable of absorbing a broad spectrum of the incident solar radiation, and having relatively lower solar to hydrogen conversion efficiencies. However, in recent years, significant advances have been made in the identification and design of novel nanomaterials with improved efficiencies and new knowledge has been produced in better understanding and unraveling of the fundamental steps and barriers that lower the quantum efficiencies in reactions or processes involving solar energy harvesting and conversion [1,2].

#### 1.1.1. Theory

Irradiation of light having energy equal or greater than the bandgap of a semiconductor on a semiconductor will eject electrons from the valence band of the semiconductor to its conduction band, leaving holes in the valence band. For example, if the bottom of the conduction band edge

is more negative compared to the $H^+/H_2$ redox couple and if the top of the valence band edge is more positive compared to the $H_2O/O_2$ redox couple, the electrons could be used to produce hydrogen at a reduction site and oxygen can be produced at an oxidation site as illustrated in Fig. 1 [3].

The excited electron-hole pair (produced typically in fs) is called exciton and they can be utilized for several applications. This novel process was first reported in 1972 by Fujishima and Honda, albeit in the photoelectrochemical mode for splitting of water into hydrogen and oxygen [4]. In this pioneering report, they irradiated a $TiO_2$ anode with UV irradiation. Oxygen was produced at the photoanode and hydrogen was produced at the Pt counter electrode. The seminal report, triggered interest in this area and since then research in the areas of photoelectrochemistry and photocatalysis have since garnered widespread attention.

#### 1.1.2. Applications of photocatalysis

Photo-excited charge carriers produced in the semiconductor upon irradiation are highly energetic species and can drive several redox reactions with water, organic compounds, metal ions, etc. As indicated in Fig. 2(a), reaction of electron with proton will produce hydrogen and reaction of hole with water will produce oxygen. In addition, to water splitting reaction, other reactions that are widely explored are conversion of solar energy into electricity, *i.e.* photovoltaics or solar cells [5–7], degradation of pollutants [8–10], and conversion of $CO_2$ [11–15] as illustrated in Fig. 2(b)–(d) [16].

Furthermore, the excitons can degrade organic pollutants discharged from textile industries [17], pharmaceutical waste [18],

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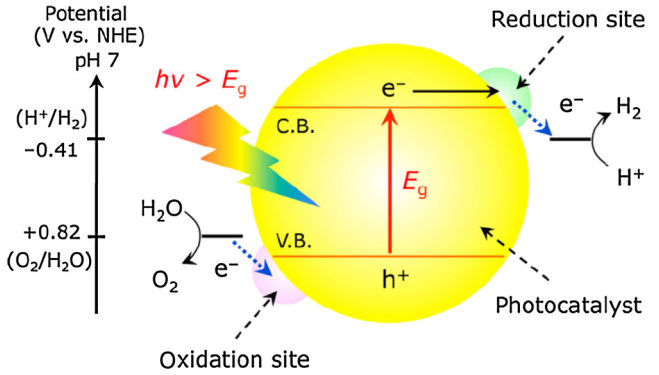


**Fig. 1.** Schematic diagram showing the photocatalytic process. Reproduced with permission from reference [3].

etc. Holes, produced by bandgap irradiation can directly or indirectly oxidize organic species and electrons, can react with oxygen which is invariably used in degradation reactions, or with surface hydroxyl groups attached to the semiconductor to ultimately produce Reactive Oxygen Species (ROS) such as hydroxyl radicals, peroxide radical, hydrogen peroxide. These ROS can react with organic pollutants to degrade them. In addition, another active area of area, lies in the application of semiconductors for antibacterial activity; this originates from the highly reaction ROS species produced, which are capable of damaging the microbial cells [19].

### 1.2. Applications of $TiO_2$ in solar energy conversion

Titanium dioxide, $TiO_2$, is an environmental friendly, inexpensive semiconductor photocatalyst that is widely available and easy to synthesize. The 3.2 eV bandgap of $TiO_2$ limits the efficient utilization of solar energy, as only a small portion of solar radiation (UV region that constitutes between 4–6%) carries photons that have energy equal or greater than the bandgap of $TiO_2$. In addition, the relatively high rate of recombination of charge carriers also limits the quantum yields.

Efforts are underway to overcome these challenges associated with $TiO_2$. These involve, making nanostructured materials in order to increase the available surface area for photocatalytic reactions and to reduce the time required for the charge carriers to reach the surface or interface thus improving the charge transfer rates. The improved charge transfer rates reflect in reduced bulk-recombination rates. In addition, efforts are also directed towards shifting the onset of absorption into the visible region. This involves depositing the photocatalysts with metallic nanoparticles [20–22], doping with transition metal ions [23], and non-metallic elements such as C [24], N [25–27], and S [28]. The dopants will introduce localized bands within the bandgap of $TiO_2$ thus red shifting the absorption spectra. Another strategy to extend the absorption into the visible spectrum is to introduce other semiconductor materials which have low bandgap [3,29,30].

#### 1.2.1. Mixed oxides

Mixed oxides are composite materials made by dispersing an active (photo)catalytic material on a support. In such mixed oxides, in addition to the individual (photo)catalytic nature of each oxide, substitution of one element in the catalyst matrix often leads to unique catalytic properties [31,32]. For example, $Ti^{4+}$ ions can substitute for $Si^{4+}$ in the tetrahedral positions of the silica framework of periodic mesoporous MCM-48 and MCM-41 materials, and enhance the photocatalytic activity for splitting of water in comparison to $Ti^{4+}$ in octahedral positions [33,34]. The support materials improve the mechanical and thermal stability, and in addition, the porosity of the support, facilitates not only the high dispersion of the (photo)catalytic active moieties, but also helps in the transport of reactant and product molecules and adsorption of pollutants [35–38].

The support material can be either periodic, *e.g.* SBA-15 [39], MCM-48 [40], CMK-3 [41], etc. or aperiodic silica, alumina, magnesia, etc. Both periodic (possessing uniform and regular arrayed of pores) and aperiodic (possessing random arrangement of pores) supports have their own advantages. For example, with periodic support, one can control the particle size of the encapsulated metal oxide to be fairly uniform, whereas on the other hand, aperiodic materials are relatively easy and inexpensive to synthesize as they do not require surfactants or structure directing agents during their synthesis.

The particle size of the photocatalyst have two major consequences in the activity: first, the optical bandgap will increase with decreasing particle size and second, the rate of bulk (volume) recombination increases with particle size. For instance, in a work on $TiO_2$-$SiO_2$ system reported by Koodali et al. [42], it has been found that there is an optimum particle size where both surface and bulk recombination reaches a minimum resulting in higher photocatalytic activity. In addition to particle size effects, for example the presence of Si-O-Ti bonds in $TiO_2$-$SiO_2$ mixed oxide system can

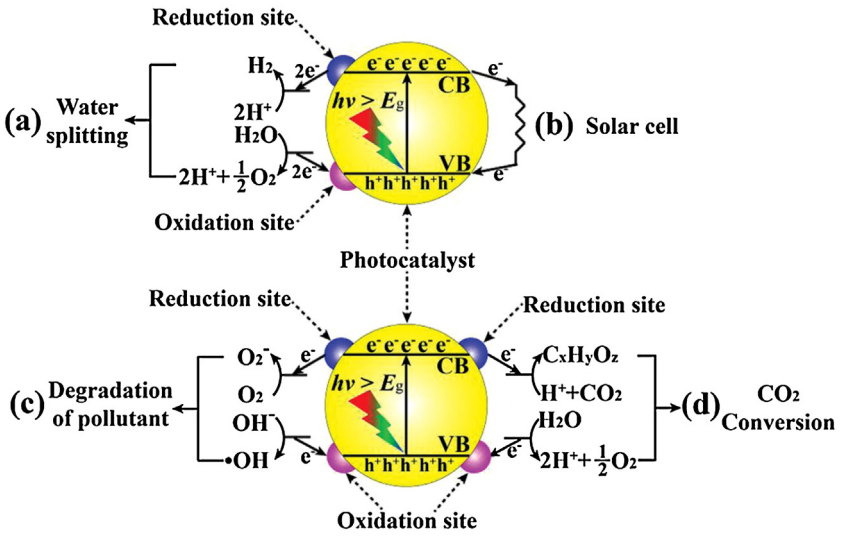


**Fig. 2.** Schematic diagram showing water splitting, solar cell, degradation of pollutants, and $CO_2$ reduction, with permission from reference [16].

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