



Non-metal doping of transition metal oxides for visible-light photocatalysis



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ABSTRACT

Transition metal oxides and mixed oxides are the largest group of materials for photocatalytic applications. Many highly active compounds are known from literature for environmental remediation, pollutant degradation and solar fuel generation. However, most of these oxides can only absorb UV light to perform photocatalytic reactions at their surface due to their large band gap. In this review, we present the recent progress in non-metal doping of transition metal oxides and mixed oxides, one of the major strategies to reduce the large band gap of semiconductor materials into the visible light range. We outline the advantages of this strategy compared to other band gap engineering methods, and especially stress the effect of efficient homogeneous non-metal doping on the optical, electronic and photocatalytic properties of photocatalysts, compared to surface doping and surface modification, including the effects of an open crystal structure on the efficiency of the doping process. We then present the highlights and breakthroughs of the last ten years in the research field and point out major improvements important for future applications, covering all the available non-metal doped transition metal oxides concerning photocatalytic reactions.

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1. Introduction

In times of an increasing demand for clean energy, global population growth and global warming, a sustainable energy production is one of the priority issues for humanity. Therefore, solar energy conversion to generate electricity or produce solar fuels is one of the major challenges scientists are facing nowadays. Hydrogen e.g. from water splitting is often discussed as future fuel as alternative to fossil fuels, especially with respect to the environmental issues of actual hydrogen production [1]. Both sunlight and water represent cheap and renewable energy sources, and the only waste product combusting hydrogen as fuel would be water [2].

While photovoltaic devices can be used to generate electricity from solar light, photoelectrochemistry and photocatalysis using semiconductor materials are direct processes converting solar light into clean hydrogen without CO₂ emission. Due to their electronic features, semiconductor materials are mostly used in photocatalysis. By using light irradiation, electrons can be excited from the filled valence band (VB) of a semiconductor into its empty

conduction band (CB) if the energy of the incident photon equals or exceeds the energy of the band gap (E_g) of the semiconductor (Fig. 1 [3–6]). After photoexcitation, the charge carriers can be separated and diffuse onto the particles surface, where they may perform redox catalytic reactions. The photoexcited negative charge carriers are strong reductants and can be used to generate e.g. hydrogen from protons, while the positive charge carriers in the VB, strong oxidants, can be used to oxidize adsorbed molecules, e.g. water to generate oxygen.

For an energetically-feasible overall water splitting reaction, the CB minimum of the semiconductor has to be more negative than the reduction potential of H⁺/H₂, while the VB maximum needs to be more positive than the oxidation potential of O₂/H₂O. This means that the E_g of the photocatalyst must be larger than 1.23 eV with appropriate band positions.

Already in 1972, Honda and Fujishima were able to perform overall water splitting using a photoelectrochemical setup [7]. However, since they used TiO₂ as light absorber, they were not able to make use of 95% of the solar spectrum: due to its E_g of 3.0 (rutile) to 3.2 eV (anatase), only UV light can be used to photogenerate charge carriers in TiO₂.

In the last decade, many different materials for photocatalytic water splitting have been prepared, and the main challenges, including broad absorption capability and reduced recombination probability, have been identified to synthesize a good material for

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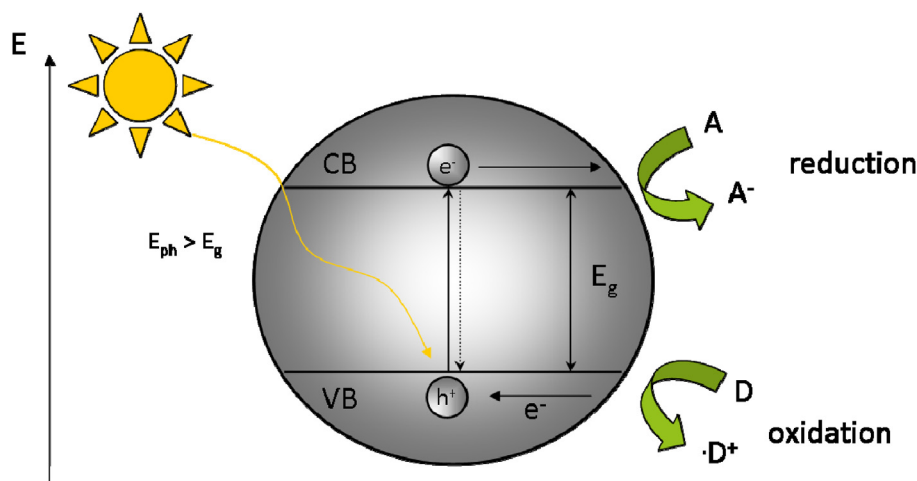


Fig. 1. Basic principle of photocatalysis with semiconductor materials (D: electron donor; A: electron acceptor).

photocatalytic water splitting by research groups all over the world [8–17]. But many of these materials still utilize only UV light for photocatalysis.

The main steps for a photocatalytic reaction are the light absorption, charge carrier separation and diffusion onto the particle surface, and the subsequent surface redox reactions with adsorbed molecules/atoms at the active sites of the photocatalyst. These steps are influenced by bulk, surface and electronic structure of the photocatalyst. Therefore, several strategies to optimize photocatalytic materials have been performed with regards to those three steps, including crystal growth and shape control [18,19], surface sensitization or modification [20–23], heterostructuring [21,24], and metal/non-metal doping [25–27] or plasmonic metallic particle decoration [28–30] for visible light absorption.

Controlling the crystal growth and shape is of special importance for particles size, crystal phase and crystallinity, all of them strongly affecting the separation of charge carriers and the efficiency of photocatalysts. Tuning the crystal shape of a photocatalyst can lead to a more efficient material when the most active crystal facets are exposed. A highly crystalline structure of the semiconductor is also advantageous for photocatalytic reactions compared to amorphous structures due to the higher mobility of excited charge carriers within the defect-free solid. One of the key tasks is therefore to synthesize materials with short diffusion length for charge carriers and abundant reaction sites by increasing the surface area. Surface sensitization and modification combine molecular or polymeric absorbers with semiconductor materials to increase the absorption range. Using a molecular sensitizer [20,21], excited electrons are transferred from the lowest unoccupied molecular orbital (LUMO) into the CB of the semiconductor (mostly TiO_2), undergoing further reduction reactions on the semiconductor surface. These systems are comparable to dye-sensitized solar cells [31], in which the sensitizer (dye) is regenerated by a redox electrolyte. With polymeric surface modification, even the formation of charge transfer complexes is possible, exhibiting direct excitation from the polymeric VB into the CB of TiO_2 [22].

If no suitable electron or hole scavenger is present on the surface, the photogenerated charges can also recombine, and the energy put into the systems is lost unused (Fig. 1). Additionally, photocatalytic water splitting comes with a large positive change in Gibbs free energy ($\Delta_R G^\circ = 237 \text{ kJ mol}^{-1}$) [10], meaning that from a thermodynamically point of view, the back reaction to water is favored and has to be inhibited. Therefore, many

examples of chemical modification of semiconductor surfaces with co-catalysts [32–36] or carbon scaffolds [37,38, and references within] (e.g. graphene) were reported, in order to retract photogenerated charge carriers from the VB or CB to spatially separate them from the semiconductor, and to inhibit recombination.

The formation of photocatalyst heterostructures or composites is another very prominent example for charge carrier separation and tuning the absorption properties of a photocatalyst. In a Z-scheme photocatalyst systems [39], two semiconductors with different absorption range are combined to drive overall water splitting via multiphoton process, and are connected via electrolytic redox shuttle. Heterostructured photocatalysts exhibiting two oxide or chalcogenide materials in close contact, both having strongly differing band positions for charge carrier separation after excitation, can readily reduce charge carrier recombination probability [24]. Thus, the lifetime of charge carriers is increased, leading to improved photocatalytic performance. It was recently shown that even a composite of two closely related Ba-tantalate crystal phases can improve the charge carrier separation dramatically [40].

Doping with metal cations, non-metal anions or non-metal molecules can strongly enhance the absorption of a photocatalyst by influencing the electronic structure of a semiconductor. The chemical state of the dopant and the location are strongly influencing the effectiveness of the doping procedure. Both options, metal and non-metal doping, have attracted much attention in the last years. Especially non-metal doping with e.g. nitrogen, sulphur and carbon has been investigated thoroughly, to decrease the E_g of wide band gap semiconductors into the visible light range.

This review focuses on the recent progress of non-metal doping of transition metal oxides, including ternary and quaternary systems, summarizing the progress in the field in the last ten years. Different doping pathways will be presented, resulting in different possibilities for the origin of visible-light activity. In contrast to other review articles, particular focus will also be given to the influence of an open crystal structure of the semiconductors on the distribution of dopants, and the resulting effects on the electronic structure of the doped photocatalyst. However, in contrast to other review articles, we will not focus on few special examples, but cover all types of non-metal doped transition metal oxide semiconductors. Homogeneous non-metal doping will be discussed as the preferable strategy for E_g tuning. Especially non-metal doped mixed oxide photocatalysts with open crystal structure will be discussed and reviewed as highly visible light active photocatalysts.

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