



Hydrogen by photocatalysis with nitrogen codoped titanium dioxide



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ABSTRACT

Titanium dioxide TiO₂ remains a benchmark photocatalyst with high stability, low toxicity and cost, but it is active only under the UV light. To increase photocatalytic activity, TiO₂ is “doped” with metals and nonmetals; nitrogen doped titania N-TiO₂ has been extensively investigated since the early 2000s. In the recent decade, an increased attention has been paid to additional dopant aka “codopant” added to N-TiO₂ to increase the photocatalytic rate. This focused critical Review covers the research on N-TiO₂ codoped with an additional element for the photocatalytic hydrogen generation, namely: (1) mechanistic studies of charge separation aimed to understand and predict photocatalytic activity; (2) nonmetal codoped N-X-TiO₂; (3) base metal codoped N-M-TiO₂; (4) noble metal codoped N-M-TiO₂. Suitability and limitations of experimental methods for characterization of codoped N-TiO₂ are discussed. The following mechanisms of photocatalysis with codoped N-TiO₂ are reviewed: (a) excitation of TiO₂; (b) excitation of N dopant induced states; c) an increased electron-hole (e-h) separation; (d) lowering over potential of hydrogen reduction; (e) excitation of the surface plasmon resonance (SPR) in N-TiO₂ codoped with nanoparticles (NPs) of noble metals. Temporal stability of codoped N-TiO₂ in H₂ generation and transformation pathways of sacrificial electron donors are discussed as well.

1. Introduction

The need for sustainable energy drives attention to hydrogen fuel [1,2]. Since the report by Fujishima and Honda [3] on water splitting, thousands of papers have been published on the topic. Titanium oxide TiO₂ remains the benchmark photocatalyst [4] for H₂ generation. The search in Web of Science (“titanium dioxide and hydrogen”) returned 3,887 hits in August 2016. Hydrogen generation with TiO₂ has been extensively reviewed [5–11]; major advantages of TiO₂ are high stability to photochemical corrosion, high activity under the UV light, low toxicity and cost. However, TiO₂ has a low absorption of light at $\lambda > 350$ nm and consequentially the low photocatalytic activity. For utilization of visible light ($\lambda > 400$ nm), it is desirable to have a strong absorption at ca. 2.0 eV (620 nm) i.e. close to the maximum in solar spectrum [12].

First, to improve absorption of visible light ($\lambda > 400$ nm) by TiO₂ [13], one can use a suitable dopant element (on surface or in the bulk) which has the high optical absorption. Second, photosensitization of the semiconductor surface with organic dyes [14] or complexes [15] is well known. While dye sensitization of solar cells was extensively studied since pioneering reports by Grätzel [16], a major problem of photosensitizer in photocatalysis is its instability to photochemical corrosion. Third, one can create nanostructures with the nanoparticles (NPs) of noble metals which absorb visible light due to plasmonic properties [17]. Major disadvantages of nanostructured photocatalysts are a high cost of nanofabrication [18] and limited stability of certain metal-titania junctions [19]. For an economically feasible price of H₂ fuel produced by photocatalysis, the cost of the photocatalyst should not be very high. Therefore, doping TiO₂ is preferred with inexpensive elements via “wet chemistry” route. In the literature, the terms

Abbreviations: AFM, atomic force microscopy; AIL, artificial inorganic leaf; AM, air mass coefficient (measure of solar irradiation); APD, arc plasma deposition; ATR-FTIR, attenuated total reflectance Fourier transformed infrared spectroscopy; BE, binding energy; BET, Brunauer–Emmett–Teller method; BJH, Barrett–Joyner–Halenda method; CB, conduction band; CBM, conduction band minimum; DEG, diethylene glycol; DFT, density functional theory; DR-TRS, diffuse reflectance time-resolved spectroscopy; EDTA, ethylenediaminetetraacetic acid; EDXS, energy dispersive X-ray spectroscopy; EF, energy of the Fermi level; e-h, electron-hole pair; EPR, electron paramagnetic resonance spectroscopy; ESR, electron spin resonance spectroscopy; EXAFS, extended X-ray absorption fine structure spectroscopy; FESEM, field emission scanning electron microscopy; FTIR, Fourier transformed infrared spectroscopy; HR-XRPD, high resolution X-ray powder diffraction; IL, ionic liquid; interstit., interstitial site; IEL, impurity energy level; ISS, ion scattering spectroscopy; LEED, low energy electron diffraction; NFT, nitrogen and fluorine doped titania; NPs, nanoparticles; NTs, nanotubes; OUES, origin unidentified energy state; PL, photoluminescence; SEM, scanning electron microscopy; SP, surface plasmon; SPR, surface plasmon resonance; STM, scanning tunneling microscopy; STS, scanning tunneling spectroscopy; subst., substitutional site; TDS, thermal desorption mass spectroscopy; TEM, transmission electron microscopy; TG-DTA, thermogravimetry-differential thermal analysis; TIPO, titanium isopropoxide; TNTs, titania nanotubes; TPD, temperature-programmed desorption; UV, ultraviolet; UV-A, light with $\lambda=315$ –400 nm; UV-B, light with $\lambda=280$ –315 nm; UV-Vis DRS, UV-Visible diffuse reflectance spectroscopy; VB, valence band; VBM, valence band maximum; VO, oxygen vacancy; XAS, X-ray absorption spectroscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; WGS, water-gas shift reaction; ZPC, zero point charge

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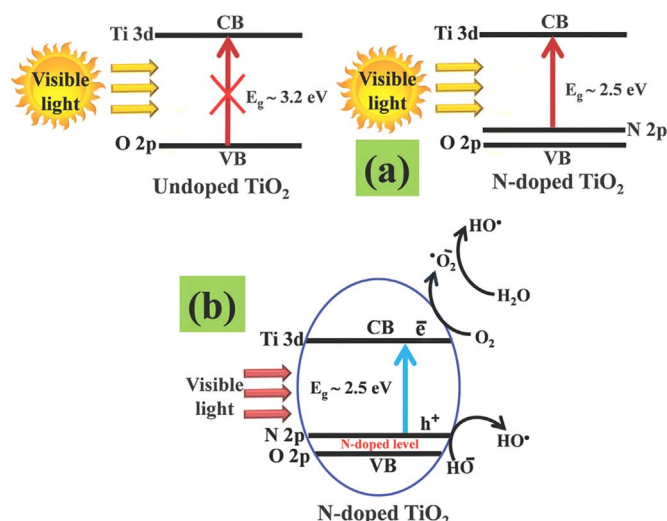


Fig. 1. (a) Energy level diagrams for undoped and N-doped TiO₂ and (b) possible reaction mechanism for the photocatalytic degradation of organic pollutants by N-doped TiO₂ under visible light irradiation. Reproduced from Ansari SA, Khan MM, Ansari MO, Cho MH. “Nitrogen-doped titanium dioxide (N-doped TiO₂) for visible light photocatalysis”, *New J. Chem.*, 2016, 40, pp. 3000–3009, with permission of The Royal Society of Chemistry (RSC) on behalf of the European Society for Photobiology, the European Photochemistry Association and the RSC. License number 3942180440172.

“dopant” and “promoter” are used interchangeably; however, not every “dopant” operates as “promoter”, since it may decrease reaction rate. For example, one can “dope” TiO₂ with cations of transition metals TM such as Cr³⁺ which has a high absorption of visible light. However, many TM dopants cause marginal improvement or even a decrease [20] of the photocatalytic rates. The substitutional site formed in TiO₂ by the TM dopant leads to oxygen vacancy V(O) which acts as charge recombination center [21] and results in a decrease in the photocatalytic rate.

One can “dope” TiO₂ with non-metals, including nitrogen which leads to N-TiO₂. Since pioneering work by Asahi et al. [22], there was a surge of interest to N-TiO₂ and nitrogen remains one of the most popular non-metal dopants [23–29]. The energy level diagram of N-TiO₂ is well studied, e.g. Ref. [26] and Fig. 1.

Recent review [25] provides main limitations of N-TiO₂ photocatalyst: (a) high concentration of N dopant is difficult to achieve due to low solubility in TiO₂; (b) an enhanced absorption and activity of N-TiO₂ could be due to, mainly, surface layers; (c) an increase in activity under visible light is moderate vs. TiO₂. These problems can be solved by an additional dopant [30] (codopant, co-dopant or “modifier”). Such photocatalysts are termed, by different authors, as nitrogen codoped TiO₂, codoped N-TiO₂, modified N-TiO₂. The review of 2010 concluded [23] that “almost all of the modified N-TiO₂ are restricted to the photodegradation of organic pollutants”.

A significant progress since mid-2000s resulted in many publications. To our knowledge, there is no review paper on photocatalytic H₂ generation with N-TiO₂ codoped with an additional element. This Review covers the following studies of codoped N-TiO₂ photocatalysts in hydrogen generation: (1) mechanisms of photoexcitation and charge recombination in codoped N-TiO₂ as a “prerequisite” to their photocatalytic activity; (2) nonmetal codoped N-X-TiO₂ (N=nitrogen, X=nonmetal); (3) metal codoped N-M-TiO₂ (N=nitrogen, M=metal not from Pt group); (4) metal codoped N-PT-TiO₂ (N=nitrogen, PT=platinum group metal). Outcomes of experimental studies are compared with models obtained from quantum chemical computations. Suitability and limitations of common experimental methods of characterization of codoped N-TiO₂ are discussed. Crystalline forms of codoped N-TiO₂ (anatase, rutile, brookite) are analyzed. Since codopant

may affect the concentration of defects in N-TiO₂, this Review discusses atomic forms of N codopant. This Review does not cover the following aspects of photocatalysis with codoped N-TiO₂: gas photocatalysis, photocatalytic degradation of pollutants in solution, photoelectrocatalytic water splitting, photocatalysis with composite structures (with at least two separate crystalline phases), and photocatalysts containing more than one codopant. The units of photocatalytic rate are important [31], but there is no standard rate unit. For convenience to the reader and in the attempt of standardization, this Review contains both originally reported rate units and units normalized per mass and total surface area of the photocatalyst, in μmol (H₂) / gram (photocatalyst) * h. (reaction). Temporal stability of codoped photocatalysts as complex materials systems is of practical importance, and we assess the stability and reuse of codoped N-TiO₂ in separate Chapter. The stability of codoped N-TiO₂ photocatalysts may be affected by products of chemical transformations of sacrificial donors which are discussed as well.

2. Experimental mechanistic studies of codoped N-TiO₂

While N-TiO₂ offers a significant decrease in the bandgap vs. TiO₂, the further bandgap narrowing is desirable which can be achieved via codoping. Both mechanistic studies of codoped N-TiO₂ (Table 1) and studies of hydrogen generation with it (Tables 2–9) involve determination of the bandgap. Sol-gel synthesis of TiO₂ from titanium alkoxides Ti-OR, including frequently used titanium isopropoxide (TIPO) proceeds via the set of chemical reactions [32] which can be simplified [33] by Eqs. (1)–(3):



In 2004, Sakatani et al. first reported [34] metal codoped N-M-TiO₂ photocatalysts. In the first step, metal-doped precursors M-TiO₂ were prepared from TIPO and metal salts via sol-gel method followed by calcination. This is also known that “nitridation” of TiO₂ with NH₃ at elevated temperatures proceeds to nitrogen-doped N-TiO₂ which can be described [35] by simplified Eq. (4):



In ref. [34], M-TiO₂ precursors were calcined in NH₃ to yield binary codoped N-M-TiO₂ photocatalysts. In photocatalytic oxidation of gaseous acetaldehyde CH₃CHO in mixture of oxygen and nitrogen (1:4) to CO₂ under visible light, N-Sr-TiO₂ showed the highest rate. Nitrogen leads to Ti³⁺ and V(O) in N-TiO₂ and absorption of visible light; an optimal concentration of interstitial Sr²⁺ decreased the concentration of defects. The N-Sr-TiO₂ contained paramagnetic N species and the EPR signal increased upon irradiation indicating their involvement in photocatalysis. In 2009, Gai et al. [36] proposed, based on the DFT calculations, the systematic codoping approach to decrease the bandgap in TiO₂ by shifting up the potential of the valence band maximum (VBM) without changing the conduction band minimum (CBM). Codoping TiO₂ with electron donor/acceptor pairs “nitrogen + vanadium” and “nitrogen+niobium” was proposed: electrons on the donor levels would passivate the holes on the acceptor levels [36]. The N-V-TiO₂ was studied in the photocatalytic oxidation of methylene blue dye in solution [37] and in CO₂ reduction in aqueous KHCO₃ into CH₄ [38], while it was not reported in H₂ generation, to our knowledge. Marchiori et al. [39] has found an increased absorbance in N-Nb-TiO₂ at 450 nm vs. N-TiO₂ and the transition diagram has been proposed by Lim. et al., Ref. [40] and Fig. 2. Niobium atom enters the substitutional

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