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Effect of band gap engineering in anionic-doped TiO_2 photocatalyst

Emy Marlina Samsudin, Sharifah Bee Abd Hamid*

Nanotechnology and Catalysis Research Center, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

A simple yet promising strategy to modify TiO_2 band gap was achieved via dopants incorporation which influences the photo-responsiveness of the photocatalyst. The mesoporous TiO_2 was successfully mono-doped and co-doped with nitrogen and fluorine dopants. The results indicate that band gap engineering does not necessarily requires oxygen substitution with nitrogen or/and fluorine, but from the formation of additional mid band and Ti^{3+} impurities states. The formation of oxygen vacancies as a result of modified color centres and Ti^{3+} ions facilitates solar light absorption and influences the transfer, migration and trapping of the photo-excited charge carriers. The synergy of dopants in co-doped TiO_2 shows better optical properties relative to single N and F doped TiO_2 with c.a 0.95 eV band gap reduction. Evidenced from XPS, the synergy between N and F in the co-doped TiO_2 uplifts the valence band towards the conduction band. However, the photoluminescence data reveals poorer electrons and holes separation as compared to F-doped TiO_2. This observation suggests that efficient solar light harvesting was achievable via N and F co-doping, but excessive defects could act as charge carriers trapping sites.

1. Introduction

The design of TiO_2 towards visible light application, especially in photocatalysis, is greatly pursued as an alternative to the conventional UV-driven TiO_2. Conventional TiO_2 consists of wide band gap of 3.2 eV and thus, limited to UV photo-excitation only. Hence, the low photocatalytic activity is inadequate for scale up industrial application. Many works have reported TiO_2 with a band gap between 3.0–3.2 eV prepared using standard physical and chemical methods with no extrinsic modification [1]. Un-modified TiO_2 has shown to be able to absorb limited portion of visible light, and is attributed to the intrinsic modification such as mixed crystal phase of anatase and rutile [2], combination of high and low surface energy crystal facets [3] and defects (i.e. Ti^{3+}, oxygen vacancy, lattice disorientation, impurities, etc.) [4,5]. However, the portion of visible light absorption was insufficient for an efficient visible-light driven photocatalytic activity [6,7].

Band gap engineering via extrinsic modifications enables larger visible light absorption relative to self-induced intrinsic modification in TiO_2 [8]. The band gap in TiO_2 can be engineered by compositing with metal oxides, hybridization with nano-materials, metal and non-metal doping and recently, hydrogenation [4,6–10]. The formation of surface hetero-junctions in TiO_2 as a result of mixed crystal phase or metal oxide composites enables visible light absorption due to smaller band gap [4,12,13]. For metal and non-metal doping, the narrowing of the band gap occurs due to the overlapping of energy states and promotes wider solar light absorption [14]. Other work observed the formation of impurities levels in the mid gap which stimulated visible light absorption [6,15]. In hydrogenated TiO_2, a significant reduction in the band gap was achieved due to the formation of band tail states from the valence band and high concentration of defects such as surface disorders and Ti^{3+}. These modifications promote visible light absorption, where some reports also demonstrated near infrared absorption as well [16–21]. In photocatalysis, the mobility of photo-excited electrons and holes is important to sustain efficient photocatalytic activity under visible light irradiation. Thus, the magnitude of band gap engineering is closely associated with the electrons and holes photo-excitation, migration and transfer process.

The preparation of visible light sensitive TiO_2 using anionic dopants of p-group elements have been studied by many [6,11,14,22–24]. The dopants include nitrogen, phosphorus, sulphur and halogen elements such as fluorine, bromine and iodine. In addition, anionic dopants are favored relative to cationic dopants such as manganese, iron, nickel and copper as the formation of deep localized d-states acting as charge traps are inhibited [9]. Furthermore, cation-doped TiO_2 shows poor thermal stability and less photochemical inertness relative to anion-doped TiO_2 [25,26]. In anionic-doped TiO_2, the band gap is engineered by the overlapping of energy states or via impurities levels created within the

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* Corresponding author.
E-mail address: sharifahbee@um.edu.my (S.B. Abd Hamid).

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mid band. Thus the type of anions plays a major role in shaping the electronic structure and tuning in the band gap for visible light driven TiO_2. For example, N-doped TiO_2 showed a band gap of 2.50–2.94 eV [27], P-doped TiO_2 showed a band gap of 2.60–3.0 eV [28,29] while halogen-doped TiO_2 reported minimal band gap changes [30]. The prepared doped TiO_2 showed visible light absorptions but with different absorption intensity. Out of all anionic dopants, nitrogen was reported as the most successful dopant to increase solar light absorption and improves the photocatalytic activity [22,31]. However, N-doped TiO_2 has been reported to suffer from rapid electrons and holes recombination as a result of bulk oxygen vacancies [6]. A decreased of activity under UV light were also observed in N-doped TiO_2 [32].

Otherwise, efficient electrons and holes separation was observed in F-doped TiO_2 owing to the highly electronegative fluorine ions decorating TiO_2 surface [33,34]. In addition, F-doped TiO_2 was reported to demonstrate better charge carriers separation relative to N-doped TiO_2 [35]. The energy level of F 2p states of fluorine is below the O 2p in F-doped TiO_2, thus does not show any band gap reduction compared to N-doped TiO_2 [30,36–38]. Besides controlled charge carrier mobility by F-doping, the growth and crystal shapes are also influenced. The incorporation of fluorine as capping agent or dopant catalyzes the formation of high surface energy facets relative to the dominant low surface energy facets of {101} in TiO_2 [3]. The creation of surface hetero-junctions between the low and high surface energy facets improves the mobility of photo-generated electrons and holes. In TiO_2 consisting of {001} and {101} facets, photo-generated electrons favorably flow from {001} to {101} and photo-generated holes from {101} to {001}. In previous work, the band gap of TiO_2 with dominant {001} facets, {111} facets and {101} facets was 3.33, 3.17, 3.16 eV respectively [39]. However, other work showed that TiO_2 with dominant {101} facets have larger band gap than those with dominant {001} facets [40]. This result demonstrates the influence of surface energy facets towards band gap engineering.

To compensate the drawbacks faced in N and F mono-doped TiO_2, co-doping of the two dopants forming N,F co-doped TiO_2 showed enhanced solar light absorption with efficient electrons and holes separation [35,41–48]. Other report stated the favorability of N,F co-doping in TiO_2 due to cost effectiveness [26]. The reported band gap of N,F co-doped TiO_2 was between 2.28 and 2.74 eV [35,45]. In previous work, the light absorption peak red shifted dramatically, relative to tail-like absorption observed in mono-doped N and F in TiO_2. The dramatic shift, which was represented by a sharp absorption edge illustrated band to band excitation under light irradiation [49]. In N,F co-doped TiO_2, the narrowing of band gap is generally attributed to the overlapping of N 2p states with the O 2p states in TiO_2, whereby F played a role to compensate the overall charge balance and induce stability of the co-doped TiO_2 [4,6,14,22,25,32,49].

It is undeniable that anionic-doping and co-doping leads to alteration of the band gap in TiO_2. However, the understanding on the effect of band structures using different anionic dopants remains ambiguous. The correlation of band gap engineering with TiO_2 morphology, crystal structure and size, exposed facets, defects and nature of doping are less emphasized. Thus this paper illustrates the phenomenon of band gap engineering for N-doped TiO_2, F-doped TiO_2 and N,F co-doped TiO_2 using various analysis and instruments such as Field emission scanning electron microscope (FESEM), energy dispersive x-ray (EDX), X-ray diffraction (XRD), diffuse reflectance ultraviolet visible spectroscopy (DRUV-vis), fourier transformed infrared (FTIR), photoluminescence (PL), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). By compiling all information, the schematic electronic structure of each photocatalysts was proposed and discussed.

2. Experimental

2.1. Materials and methods

All of the chemicals were purchased from Sigma Aldrich and used without further pre-treatment. These chemicals include titanium isopropoxide (97%), hydrochloric acid (37%), absolute ethanol, pluronic F127, triethylamine (99%), trifluoroacetic acid (98%) and ammonium fluoride (98%). Milli-Q deionized water was used throughout the experiments.

Four types of photocatalysts were prepared using surfactant assisted sol-gel method. Mixture A: 2.20 g of pluronic F127 was added to 40 ml of deionized water and ethanol mixtures. The pH of this mixture was adjusted to 3.7 accordingly. Mixture B: A premix of titanium isopropoxide (TTIP) precursor and 50 ml of absolute ethanol was prepared and added dropwise into mixture A under vigorous stirring. The sol was left to aged overnight and the formed gel was dried at 85 °C and yellow sand-like granules were formed. The grinded granules was calcined under continuous air flow at 500 °C for 6 h to obtain mesoporous TiO_2. For the preparation of doped samples using an initial molar ratio of 0.5, 2.47 ml of triethylamine (N precursor), 1.36 ml of trifluroacetic acid (F precursor) and 0.66 g of ammonium fluoride (N,F precursor) were added in mixture A, respectively. Similar ageing, drying and calcination steps were applied. The four photocatalysts were labelled as TiO_2 (un-doped), N-TiO_2 (nitrogen-doped), F-TiO_2 (fluorine-doped) and N,F-TiO_2 (nitrogen and fluorine doped simultaneously).

FESEM Quanta FEI 200F was used to analyze the surface morphology, size and particles distribution using magnification between 50 and 200 k. The elemental compositions of each photocatalysts were analyzed by energy dispersive x-ray spectroscopy (EDX). The BET surface area and pore size were measured using nitrogen adsorption-desorption analyzer. Bruker AXS D8 X-ray diffraction (XRD) with a Cu Kα radiation was used to analyze the crystal structure, crystallite size and crystal ratio. The crystal structure was matched against JCPDS of 731764 and 340180 representing anatase and rutile respectively and the ratio was estimated by Spurr's equation [50]. PL-Raman spectroscopy was used to confirm on the chemical structure, concentration of exposed low and high energy facets and charge carriers behavior. LabRam confocal Raman microscope with 325 nm line of continuous He-Cd laser at room temperature was applied. Bruker 80/80 v Fourier transformed infrared (FTIR) was used to evaluate the functional groups and any impurities from 450 to 4500 cm^{-1}. The optical response was analyzed by diffuse reflectance ultraviolet visible spectroscopy (DRUV-vis, Agilent Cary 100). The band gap of each samples were estimated using Kubelka-Munk theory [51]. X-ray photoelectron spectroscopy (XPS, Thermo scientific K-alpha instrument) was used to investigate the surface chemical properties with the XPS core level aligned to C 1s of 285 eV. The samples were observed using a non-mono-chromatized Mg Kα with photon energy of 1253.6 eV.

A custom built stirred tank photo-reactor equipped with UV (6–20 W, $\lambda < 350$ nm) and visible light (150 W, λ at 1000 nm with UV cut off filter of 420 nm) lamps were used for the photocatalytic degradation of 0.5 mg/l atrazine pollutant. The photocatalyst loading was fixed at 0.5 g/l and no pH adjustment was done throughout the experiment of 180 min. The catalyst was left to stir in darkness for 30 min to optimize atrazine absorption on the surface of the catalyst. In addition, no photolytic effect was observed for photodegradation of atrazine in the absence of catalyst (result not shown here). The temperature of the photo-reactor was kept constant by using a circulating water bath. During the experiment, optimum contact between the photocatalyst and pollutant was achieved by constant stirring at 420 rpm. Filtered samples were taken every 30 min interval and analyzed using Perkin Elmer UV–vis analyzer. The maximum absorption wavelength for atrazine

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