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Development of photocatalyst by combined nitrogen and yttrium doping

Matiullah Khan [a,b], Wenbin Cao [a,*]

[a] Department of Inorganic Nonmetallic Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, 100083 Beijing, China
[b] Department of Physics, University of Science and Technology Bannu, 28100 Bannu, Pakistan

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ABSTRACT

Titanium dioxide co-doped with yttrium and nitrogen with different yttrium doping concentration has been synthesized by mild one pot hydrothermal method without any post calcination for crystallization. Irrespective of the yttrium doping concentration, all the synthesized samples were composed of pure anatase phase with good crystallinity. And the synthesized co-doped samples have spherical morphology with uniform particle size distribution. The absorption edge of the co-doped TiO_2 was shifted toward visible light region depicting that the intrinsic band gap of TiO_2 was affected by the co-doping. Among the different samples, the co-doped sample with 0.05% yttrium doping concentration exhibits enhanced visible light photocatalytic activity by degradation of methylene blue in aqueous solution. Compensated and non-compensated yttrium–nitrogen co-doped TiO_2 models were simulated using density functional theory to explain the experimental findings. The calculation results show that the compensated yttrium–nitrogen co-doped TiO_2 model may reasonably explain the experimental observations due to its stable configuration, narrowed band gap and enhanced separation of photoexcited carriers.

1. Introduction

Visible light active TiO_2 based photocatalysis has received increasing attention from researchers in recent years due to its wide potential applications in photoelectrochemical processes. The photocatalytic process on TiO_2 surface depends on many factors including its band gap, following with visible light absorption, life time of the photogenerated carriers and oxidizing species at TiO_2 surface [1–3]. Doping foreign atoms in TiO_2 can improve the photocatalytic properties of TiO_2 by tailoring its electronic band structure [4–6]. The effort to get visible light active photocatalyst with higher efficiency starts from the report published by Sato [7], who argued that introducing NO_x species in TiO_2 could narrow the band gap and lead to visible light absorption. After Asahi et al. [8] published their work in Science, nitrogen doping was found to be a promising method for reducing the band gap of TiO_2. Nitrogen doping in TiO_2 has been widely studied using both experimental and theoretical techniques and has been proven it is a reasonable way to improve the photoelectrochemical properties of TiO_2 [9–11]. However, most researchers agree that N doping creates N 2p states above the valence band maximum which annihilates the electron–hole pairs [12,13]. Besides nitrogen doping, rare earth ions doped TiO_2 has also been found to be a promising way for shifting the absorption edge of TiO_2 toward visible light region and improving its photocatalytic efficiency under visible light irradiation [14]. Among which yttrium doping in TiO_2 lattice was found to be successful in shifting the absorption edge of TiO_2 toward visible light region, reducing the rate of electron–hole pair's recombination and improving its photoactivity compared to that of un-doped TiO_2 [15–17]. Recently, the concept of metal non-metal co-doping in TiO_2 was introduced and identified for improving the visible light absorption and the photocatalytic activity of TiO_2 compared to mono (metal/non-metal)-doped TiO_2 [18,19].

Non-metal doping is effective in inducing visible light absorption while the metal dopant can enhance the electron–hole pair's separations, so their combined effect can synergistically improve the photocatalytic activity of TiO_2 [20]. Zhang et al. [20] codoped TiO_2 with yttrium and nitrogen using sol–gel method. The codoped sample improved the photocatalytic activity compared to mono-doped samples. The enhanced photocatalytic activity of the

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[*] Corresponding author at: Department of Inorganic Nonmetallic Materials, School of Materials Science and Engineering, University of Science and Technology Beijing (USTB), 30 Xueyuan Road, Haidian District, Beijing 100083, PR China. Tel.: +86 10 62332457; fax: +86 10 62332457.
E-mail address: wbcao@ustb.edu.cn (W. Cao).

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co-doped sample was attributed to the synergistic effect of co-doping [20]. However, the synergistic effect caused by the codopants on the improved visible light photocatalytic activity has not yet been clarified [20]. Moreover, it is necessary to investigate corresponding variations in the photocatalytic properties of the co-doped sample due to the changing of the Y doping concentration. The effects of both the low and high Y doping concentration in the (Y, N) co-doped TiO_2 on its photocatalytic properties has not yet been investigated and the main cause of the improved photocatalytic activities is still not clear. Furthermore, some reasonable, cheap and quick methods should also be sought for the synthesis of (Y, N) co-doped TiO_2 photocatalyst.

Lin et al. [21] simulated Y-doped TiO_2, N-doped TiO_2 and (Y, N) co-doped TiO_2 systems based on density functional theory (DFT). It was found that Y, N co-doping reduced the band gap of TiO_2 and induced visible light absorption [21]. However, the authors only considered noncompensated (Y, N) co-doped model without considering the charge compensation due to the creation of oxygen vacancy or interstitial nitrogen atom. Experiments show that yttrium often replaces lattice Ti^{4+} at its +3 oxidation state [20], so this charge instability should be compensated for getting stable atomic configuration. The formation energy of oxygen vacancy is comparatively lower than that of Ti vacancy, so the most probable compensation should be done by the creation of oxygen vacancy [21]. For reasonable explanation of the experimental observations, both compensated and noncompensated (Y, N) co-doped systems should be introduced. Widely reported in literature, doped N in the N-doped TiO_2 either replaces lattice O atom or resides at interstitial sites [22]. So, the doped N in the (Y, N) co-doped TiO_2 has the chances of either replacing lattice O or going to the interstitial position between the atoms. For a better comparison with the experiments, the calculations should be performed for both interstitial N and substitutional N in the (Y, N) co-doped TiO_2 for compensated and noncompensated cases.

In this paper, (Y, N) co-doped TiO_2 with different Y doping concentration (both high and very low) has been synthesized by mild one pot hydrothermal method without any post calcination for crystallization. Doped samples shifted their absorption edges of TiO_2 toward visible light region and among the different samples, 0.05% (Y, N) co-doped TiO_2 possesses the best photocatalytic performance to decompose methylene blue under visible light illuminations. To explain the experimental observations, both compensated and noncompensated (Y, N) co-doped TiO_2 systems with different location of the doped atoms were simulated based on density functional theory. The theoretical calculations may reasonably explain the experimental observations.

2. Experiments and calculations

2.1. Experiments

The mild one pot hydrothermal method was used to synthesize pure and co-doped samples without any post calcination for crystallization. $TiOSO_4$, $(NH_2)_2CO$, $Y(NO_3)_3{\cdot}6H_2O$ and guanidine hydrochloride with different ratios were mixed with known amount of water to synthesize (Y, N) co-doped TiO_2 with different Y doping concentration. In the preparation of different (Y, N) co-doped TiO_2 samples, the amount of other precursors were kept constant and only the amount of $Y(NO_3)_3{\cdot}6H_2O$ was varied to investigate the effect of Y doping on the photocatalytic properties of (Y, N) co-doped TiO_2. The known amount of precursors were mixed with distilled water in a 100 mL internal volume autoclave and then heated at 150 °C for 8 h. The obtained precipitates were washed repeatedly with distilled water till the pH of the rinsed water became 7.0. The precipitates were extracted from the liquid and then dried in air to obtain the (Y, N) co-doped TiO_2. Based on Y doping concentration, the different samples were named as 0.01% (Y, N)–TiO_2, 0.05% (Y, N)–TiO_2, 0.1% (Y, N)–TiO_2 and 1.38% (Y, N)–TiO_2 containing 0.01, 0.05, 0.1 and 1.38 at% yttrium, respectively. The nominal nitrogen concentration in each codoped sample was kept constant as the experimental processing parameters were kept unchanged therefore the relative effect due to N dopant has been naturalized. Pure TiO_2 was synthesized following the same procedure without adding Y $(NO_3)_3{\cdot}6H_2O$ and guanidine hydrochloride in the initial suspension.

The as-synthesized samples were characterized using XRD, TEM, XPS, UV–vis absorption spectra and their photocatalytic activity under visible light irradiation were evaluated. XRD (HZG41B, DMAX-RB, 40 kV, 30 mA, Cu Kα radiation) was used to identify the phase composition and crystallinity of the samples. The crystallite size of the synthesized samples was calculated by Scherrer's formula. TEM (Hitachi, Jeol-200CX), BET (Quanta Chrome, NOVA 1000-TS) and XPS (VG, Escalab, MK II) were used to investigate the particle size and morphology, specific surface area and the composition/chemical states of the samples, respectively. The UV–vis absorption spectra (TU-1901) of all the samples were evaluated to observe the shift in the light absorption edge. The visible light photocatalytic activity was evaluated by mixing 1 g of the sample with 100 mL aqueous solution of methylene blue (MB) having concentration of 10 mg/L. After stirring the suspension to make equilibrium between adsorption/desorption of MB, it was illuminated to a light source having illumination intensity of 5.80 mW/cm^2 reaching surface of the solution with the emission spectrum of 400–650 nm. After each 2 h interval during the degradation process, known amount of suspension was sampled from the MB suspension. Finally, the TiO_2 particles were centrifuged from the suspension and the absorption performance of the separated solution was tested by TU-1901 UV–vis spectrometer.

2.2. Calculations

Supercell model was used for performing calculations for pure and different doped models. Pure anatase TiO_2 unit cell has four Ti atoms and eight O atoms, which is extended to $3 \times 2 \times 1$ repetition having 72 atoms in total. Single N doped and Y doped models were introduced by substitutionaly doping N and Y atoms at O and Ti sites, respectively. Besides mono-doping, different (Y, N) co-doped systems were introduced to explain the experimental observation. For (Y, N) co-doped model, three different configurations of the doped atoms were introduced for investigating the effect of relative dopant location on the stability, electronic and optical properties. The N and Y atom were substitutionaly doped at O and Ti sites having distance of 2.524, 6.495, and 8.722 Å forming Model A, B and C, respectively. Model B provides the most stable configuration and the best electronic band structure among the three different models.

To investigate (Y, N) co-doped system in detail, different compensated and non-compensated co-doped systems were introduced. Experiments about N-doped TiO_2 show that doped N either occupies the substitutional or interstitial position in the TiO_2 lattice [22]. Co-doped systems with different position of the doped N were modeled to elucidate the effect of doped N in the electronic and optical properties of (Y, N) co-doped TiO_2. In the co-doped system, Ti was replaced by Y and different locations for the N atom were selected. Nitrogen was doped substitutionaly at O site and at interstitial position resulting in two different co-doped models represented by YN_{SUB}–TiO_2 and YN_{INT}–TiO_2, respectively. Y doping in TiO_2 causes oxygen vacancies for charge compensation [20]. In order to take into account the probable effect due to the oxygen vacancies, different compensated (Y, N) co-doped systems with oxygen vacancies were modeled. One oxygen vacancy was