### Multiple dopants induced spatial bandgap engineering of TiO2 for enhanced photocatalytic dye degradation

Enjun WANG, Yaan Cao\*

Nankai University , 300457 China

### Abstract

Indium, tin, and nitrogen co-modified titania photocatalysts were synthesized by a simple sol-gel technology. Tin was weaved into titania matrix in substitutional mode, while nitrogen and indium exist as surface structure (O-N and Cl-In-O). The doping and surface states energy levels of tin, nitrogen, and indium are located inside the band gap. Thus the co-modification of nitrogen, indium, and tin could largely improve the absorption in the visible light region and impede the recombination of photoinduced carriers. This indicates that co-modification titania is a promising way to enhance the photocatalytic dye degradation activity.

### Introduction

Titania has been investigated extensively as high-performance photocatalyst for energy source and environmental applications, owing to its high chemical stability and good photocatalytic effect.[1-5](#_ENREF_1) However, the photocatalytic performance is still limited owing to the large band gap, and the high recombination efficiency of photoinduced charge carriers. To improve the photocatalytic ability of titania-based photocatalysts, doping with metal or non-metal elements,[3](#_ENREF_3), [6-12](#_ENREF_6) has become one of the prevailing means to fully utilize solar light. It is reported that the Sn4+ doping can improve the photocatalytic performance of titania under visible light irradiation by promoting the separation of photogenerated charge carriers and extending the absorption to the visible region.[13](#_ENREF_13)

Moreover, the visible-light absorption and photocatalytic effect could be further improved for a photocatalyst with multi-dopants, [14](#_ENREF_14),[15](#_ENREF_15),[16](#_ENREF_16) ,[17](#_ENREF_17), because of the contribution derivative from all the dopants. The unique chemical structure, Cl-In-O is shown on the surface of titania and the surface states energy level is located at 0.3 eV below the conductive band of titania, leading to an improvement of the visible light absorption and an efficient separation of charge carriers. However, the formation mechanism of surface structure and doping mechanism of the dopants are not yet fully explored up. At the same time, combining doping and modification with dopants shows promising prospect in catalysis.

Herein, a new type of photocatalyst co-modified with indium, nitrogen, and tin is prepared using a simple sol-gel technology. Tin is waved into the titania matrix in substitutional mode, while indium and nitrogen exist as surface structure. Furthermore, this photocatalyst exhibits noticeable high photocatalytic activity. The doping behavior and mechanism of photocatalysis are also discussed detailly.

### Experimental Section

* 1. **Catalyst synthesis.**

The synthesis of multiple dopants modified photocatalysts was carried out as follows. Specifically, InCl3 (1 mol L-1, 1-5 mL for the samples with different In concentration) solution mixed with 60 mL ethanol was stirred in room temperature. The resulting solution was added with Ti(OC4H9)4 (18 mL, 99 %) and concentrated HCl solution (8 mol L-1, 1 mL). The resulting mixture was stirred continuously for 30 min, SnCl4 aqueous solution (2 mL) and ammonia (1 mL) were added. The formed white precipitation was carefully recovered by centrifugation and annealed at 800K for 3 hours. Pure TiO2, nitrogen doped TiO2 (TiO2-N), nitrogen and indium doped TiO2 (TiO2-N-In) are prepared by the similar procedure, with corresponding minor changing according to the aiming photocatalyst.

* 1. **Characterization**

The XRD characterization was acquired on a Siemens D-500 X-ray diffractometer with Cu Kradiation. The average crystallite size was calculated from the Scherrer formula (*D* = *k* /*B* cos**). Nitrogen adsorption–desorption isotherms were obtained on a Micromeritics TriStar 3000 porosimeter at 77 K. All samples were outgassed at 130oC for 8 h under vacuum prior to measurements. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a KRATOS Axis Ultra. Raman spectra were taken on a Raman spectrometer (Ahura First Defender XL) using the 532 nm line as the excitation source. Diffuse reflectance UV–visible absorption spectra were collected on a Varian Cary 5 spectrophotometer.

* 1. **Evaluation of Photocatalytic Activity**

The photocatalytic degradation of p-chlorophenol was carried out in a 70 mL glass reactor with 15 mg of photocatalyst suspended in p-chlorophenol solution (50×10-6 mol L-1, 60 mL) under irradiation. A 600W Xe lamp was used as the light source, and a 390-nm filter was utilized to remove ultraviolet light. The reactor was perpendicular to the light beam and located 15 cm away from the Xe lamp. The p-chlorophenol solution was constantly bubbled by O2 gas at a flux of 3 mL min-1 under stirring at room temperature. Every two hours the residual concentration of p-chlorophenol was measured by a UV-visible spectrometer (SHIMADZU UV--2010PC). Prior to photocatalytic reactions, the suspension was stirred in the dark for 30 min to reach the adsorption equilibrium of the p-chlorophenol molecules.

### Results

**Photocatalytic activity**



Fig.1 Photocatalytic activity of TiO2, TiO2-N, TiO2-N-In, and TiO2-N-In-Sn, (A) under visible light irradiation; (B) under UV-light irradiation.

The liquid−solid photocatalytic activities of the prepared photocatalyst were evaluated by using p-chlorophenol as a model of pollutant. Fig. 1, Table1 and Table 2 show the photocatalytic degradation results. For all of the samples, the ln(*c0/c*) values of p-chlorophenol linearly relates to the irradiation time, suggesting a pseudo-first-order kinetics.

Under visible light irradiation ( > 390 nm) for 8 hours (Fig.1A and Table 1), the p-chlorophenol can hardly be degraded. Only a little p-chlorophenol has been decomposed in the presence of TiO2. TiO2-N and TiO2-N-In exhibit better photocatalytic activity and about 20.0 % and 29.0% of p-chlorophenol was decomposed, respectively. For TiO2-N-In-Sn sample, nearly 90.0% of p-chlorophenol has been decomposed, whose photocatalytic activity (photodegradation rate and specific photocatalytic activity) is almost 4 and 3 times that for TiO2-N and TiO2-N-In, respectively. Under UV light irradiation (shown in Fig.1B and Table 2), the co-modified TiO2 sample still shows a much better photocatalytic activity than TiO2, TiO2-N, and TiO2-N-In samples. These results suggest that the doping of Sn4+ ions into the TiO2-N-In system is an effective method to improve the photocatalytic performance. The enhancement mechanism will be discussed in the following sections.

**Table 1.** The photodegradation of p-chlorophenol under visible light irradiation (λ>390nm).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Degradation  ratio**a**(Δc/c0) | k **b**/min-1 | t1/2/min | Specific photocatalytic  activity/(mol•g-1•h-1) |
| Blank **c** | 0.035 | 7.42×10-5 | 9338.7 | — |
| TiO2 | 0.097 | 2.11×10-4 | 3275.0 | 6.04×10-5 |
| TiO2-N | 0.212 | 4.97×10-4 | 1393.5 | 1.32×10-4 |
| TiO2-N-In | 0.280 | 6.84×10-4 | 1012.8 | 1.75×10-4 |
| TiO2-N-In-Sn | 0.907 | 4.95×10-3 | 140.0 | 5.67×10-4 |

**a After reaction for 8 h. b Apparent rate constant deduced from the linear fitting of ln(c0/c) versus reaction time. c** **The blank experiment is carried out without a catalyst under otherwise identical conditions.**

**Table 2.** The photodegradation of p-chlorophenol under UV light irradiation**.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Degradation  ratio**a**(Δc/c0) | k **b**/min-1 | t1/2/min | Specific photocatalytic  activity/(mol•g-1•h-1) |
| Blank **c** | 0.043 | 7.25×10-4 | 955.3 | — |
| TiO2 | 0.335 | 6.79×10-3 | 102.1 | 1.67×10-3 |
| TiO2-N | 0.900 | 3.84×10-2 | 18.1 | 4.50×10-3 |
| TiO2-N-In | 0.720 | 32.12×10-2 | 32.7 | 3.60×10-3 |
| TiO2-N-In-Sn | 0.960 | 5.36×10-2 | 12.9 | 4.80×10-4 |

**a After reaction for 1 h. b Apparent rate constant deduced from the linear fitting of ln(c0/c) versus reaction time. c The blank experiment is carried out without the catalyst under otherwise identical conditions.**

### Discussion



Fig. 2 XRD patterns of TiO2 (a), TiO2-N (b), TiO2-N-In (c) and TiO2-N-In-Sn (d). Inset is the enlarged XRD peaks of the crystal plane (1 0 1).

The modification mechanism is closely related to the crystal structure, which has been studied by XRD. Fig.2 shows the XRD patterns of all the samples. It can be clearly observed that the majority of crystallite phase is anatase for all samples and no other phase, like rutile, In2O3, and SnO2 are observed. The inset in Fig.2 displays the magnified (101) peaks for all the samples. In comparison to pure titania, TiO2-N and TiO2-N-In show no shift of the (101) peaks, while multiple modified sample does displays a lower diffractive angles shift of (101) peak. The diffraction peaks of crystal planes (1 0 1) and (2 0 0) in the curves are refined to determine the lattice parameter and crystal size of all samples (Table 3). We can find that the cell volumes of TiO2-N-In and TiO2-N are almost the same as pure titania, while that of TiO2-N-In-Sn becomes much larger.

**Table 3** Lattice parameters and crystal size of the samples refined with rietveld method.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | cell parameters (Å) | | cell volume  (Å3) | crystal size(nm) | *S*BET  (m2 g-1) |
| *a* =*b* | *c* |
| TiO2 | 3.784 | 9.501 | 136.03 | 12.9 | 68 |
| TiO2-N | 3.786 | 9.497 | 136.16 | 12.2 | 76 |
| TiO2-N-In | 3.785 | 9.489 | 135.97 | 10.2 | 82 |
| TiO2-N-In-Sn | 3.795 | 9.508 | 136.97 | 9.4 | 114 |

The existing states of the alien element are mainly determined by two factors: electronegativity and ionic radius of the doping ions.[11](#_ENREF_11), [13](#_ENREF_13) If these features of the alien atoms match those of the hostel materials, it is feasible for the alien atoms to enter into the host materials in substitutional mode.[13](#_ENREF_13) For nitrogen atoms, since its radius (172 pm) is greatly larger than that of oxygen (139 pm)[18](#_ENREF_18), a dramatic change in lattice parameter and cell volume would be expected for substitutional case, which is not observed in the results above. The substitutional doping case could thus be excluded. Hence, nitrogen atoms are supposed to exist as titania surface structure.

The doping of alien atoms in titania is reported to show two different kind of behaviors: interstitial and substitutional doping.[13](#_ENREF_13) The first case is applied to the elements with the ionic radius relative smaller. As the ionic radiuses of both In3+ ion (81 pm)[19](#_ENREF_19) and Sn4+ ions (69 pm)[18](#_ENREF_18) are pretty large[13](#_ENREF_13), the substitutional case should be excluded. For the latter case, an increase of lattice space with a shift to lower angles of XRD peaks is expected for relatively big alien atoms. Based on the above mechanism, the In exists in substitutional mode could be excluded. We could observe an enlarged matrix space for the lattice parameters for TiO2-N-In-Sn. Therefore, based on the results of XRD, we can deduce that tin have entered into the TiO2 matrix in substitutional mode, while both indium and nitrogen exist as surface structure. With the introduction of alien elements, we could also observe the decrease of the crystal sizes.



Fig.3 XPS spectra of N1s (a), In3d (b), Cl2p (c) and Sn3d (d) for TiO2-N-In-Sn sample.

XPS measurements are used to investigate the bonding environment of nitrogen, indium, and tin in the co-modified sample. In Fig.3a, the nitrogen peak of TiO2- In-Sn-N at around 399.9eV is consistented with reported results.[20](#_ENREF_20), [21](#_ENREF_21),[22](#_ENREF_22),[23](#_ENREF_23) also, the peak at 400.1eV could be attributed to the O-N structure formed on the surface of titania.[24](#_ENREF_24)

Fig.3b and Fig.3c show the In 3d and Cl 2p spectra of a typical Cl-In-O structure formed on the surface of TiO2.[15](#_ENREF_15), [25](#_ENREF_25), [26](#_ENREF_26) The peak position of In3d5/2 (445.4eV) lies between that of in In2O3 (444.5 eV)[27](#_ENREF_27) and InCl3 (445.6 eV)[28](#_ENREF_28). For the Cl spectra of TiO2-N-In-Sn (Fig.3c), the peak position of Cl2p3/2 lies between TiCl4 and InCl3. We could thus infer that the doped In3+ ions might connect with the O and Cl ions simultaneously, leading to the formation of a Cl-In-O configuration on the surface of titania.

Fig.3d presents the Sn3d result of TiO2-N-In-Sn and the peak around 486.8eV is ascribed to the substitutional Sn. Hence, we could deduce that both the introduced indium and nitrogen exist as surface structure (Cl-In-O and O-N structure), while tin in substitutional mode..

Scheme 1. Proposed mechanism for the formation of surface structure.



The doping mechanism could be explained as follows. During the gelation process for pure titania, one Ti ion which links with six hydroxyls would dehydrate and condense with another Ti ion to form Ti-O-Ti structure.[31-33](#_ENREF_31) After the introduction of the dopants, the doped ions (R) that usually links with four hydroxyls would also condense with the Ti-OH:

HO-Ti + HO-R → Ti -O- R

The condensation possibility of hydroxyl is closely related to the ionic potential of the alien ions. In the case of tin-TiO2, as the ionic potential of Ti4+ is bigger than In3+ (0.058 vs. 0.038), the condensation possibility of hydroxyl connected to tin is less than that for titanium. Also, if the HO-In3+ condenses with more than one HO-Ti4+, it would be much harder for another hydroxyl of In3+ to get condensed. However, as the ionic potential for titanium is almost the same for tin (0.056 vs. 0.059), it is earlier for tin to enter into the matrix during the condensation process, which accounts for the different doping behavior. Likewise, surface O-N structure also follows the similar formation mechanism.



Fig.4 Diffuse reflectance UV-vis spectra of the samples. The inset gives the differential DRS spectra of TiO2-Sn.

The electronic band structure and alien energy level are closely linked to the photogenerated carriers transferring process and photocatalytic activity. Fig.4 shows the ultraviolet-visible diffuse reflection absorbance spectra of all the samples. Pure titania displays the band-band transition strong absorption,[16](#_ENREF_16) whose absorption onset edge is about 410nm, corresponding to a band gap of 3.02eV. Compared to the pure titania, TiO2-N exibit a tailing hump absorption in visible resion, arising from carriers transition from conductive band to the alien energy level.[34](#_ENREF_34), [35](#_ENREF_35) The multiple-modified sample displays the strongest absorption in visible resion.



Fig.5 Fluorescence spectra of pure TiO2, TiO2-N, TiO2-N-In and TiO2-N-In-Sn

The photocatalytic activity is closely related to the transferring behavior of the photogenerated electrons and holes.[37](#_ENREF_37), [38](#_ENREF_38), [35](#_ENREF_35) Fig.5 shows the fluorescence spectra of all the samples, we could observed that with the introduction of alien atoms, the peak Intensity decrease as a result of the introduced energy level acting as carriers trap.

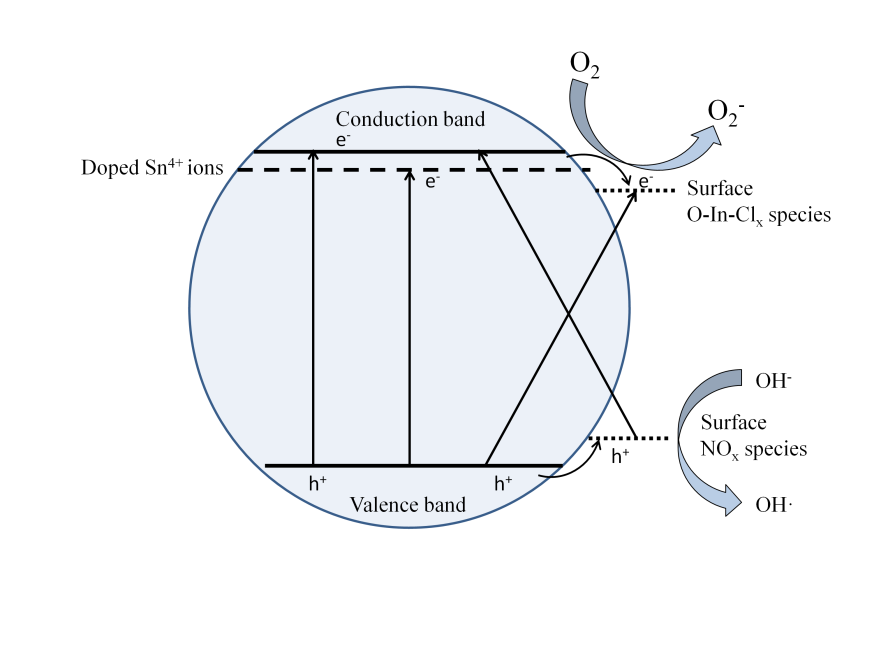


Fig.6 Schematic diagram of the photocatalytic mechanism for nitrogen and indium co-modified titania.

On account of the aforementioned results, the reason that TiO2-N-In-Sn exhibits the best photocatalytic activity on the degradation of p-chlorophenol under both visible and UV light irradiation could be explained (Fig.6). As for visible light, pure titania can hardly be excited due to its large band gap, which leads to a poor visible-light photocatalytic degradation performance. After modification with nitrogen, electrons can be excited directly from the surface state energy level of O-N surface structure to the conduction band, as the surface state energy level of O-N structure locate at 0.25eV above the valence band of TiO2. Moreover, the O-N surface structure can also act as hole trapping centers, inhibiting the recombination of photoinduced carriers. As a consequence, compared to pure TiO2, the activity of TiO2-N is obviously improved under visible light irradiation.

For TiO2-N-In, the formation of O-N structure and Cl-In-O structure contribute to the photocatalytic activity synergisticly, leading to improved activity. For multiple-modified sample, besides the contribution of surface structure (O-N and Cl-In-O structure), electrons can also be excited from the conductive band to the tin energy level, leading to the best photocatalytic degradation activity.

### Conclusion

In conclusion, for utilizing solar light more efficiently, a new type of titania-based photocatalyst (TiO2-N-In-Sn) has been prepared by modifying TiO2 with nitrogen, indium, and tin. The TiO2-N-In-Sn sample exhibits a much improved photocatalytic activity than pure TiO2, TiO2-N, and TiO2-N-In under irradiation. The modification mechanism of tin nitrogen and indium is also investigated detailly in this work. It is expected that further research on multiple elements co-modified titania would be carried out to move forward the photocatalytic research.

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