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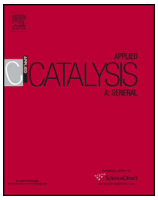

# Indium doped and carbon modified P25 nanocomposites with high visible-light sensitivity for the photocatalytic degradation of organic dyes

Zheng Jin[a], Wei Duan[a], Wubiao Duan[a,*], Bo Liu[a], Xidong Chen[a], Feihua Yang[b], Jianping Guo[b]

[a] *Department of Chemistry, School of Science, Beijing Jiaotong University, Beijing 100044, China*
[b] *State Key Laboratory of Solid Wastes Resource Utilization and Energy Saving Building Materials, Beijing Building Materials Academy of Sciences Research, Beijing 100041, China*

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## ABSTRACT

The commercially available $TiO_2$ Degussa P25 was modified using a simple technique to produce a visible-light-actived indium and carbon doped P25 catalyst. The modified photocatalysts have been successfully obtained by thermal heating method. These as-obtained products were successfully characterized by X-ray diffraction (XRD), X-ray photoelectrion spectroscopy (XPS), scanning electron microscope (SEM), high resolution transmission electron microscopy (HRTEM), UV–vis diffuse reflectance spectroscopy (DRS) and photoluminescence (PL) spectroscopy respectively. The photocatalytic activities of all prepared catalysts were evaluated by the degradation of organic dyes including methylene blue (MB) and Reactive Red 4 (RR4) under visible light irradiation. As the result shown, the indium and carbon co-doped on P25 nanocomposites possessed the extended light absorption in visible light and better charge separation capability as compared to the pristine P25. The optimum loading of $In^{3+}$ ions on P25 was 15%. Moreover, 15% $In_2O_3$/C-P25 showed the highest degradation rate of organic dye, which the removal efficiency can reach over 90% after 90 min and the corresponding hydrogen evolution rate of 15% $In_2O_3$/C-P25 was 9 times than P25. It was concluded that the synergistic effects of $In^{3+}$ ions and carbon narrowed the band gap of $TiO_2$ and promoted charge separation, which played a significant role for the enhancement of photoactivity. In addition, it was observed that the photo-degradation for all catalysts followed the first order reaction kinetics. Furthermore, the influence of initial pH values on the photocatalytic degradation of MB and RR4 using 15% $In_2O_3$/C-P25 catalyst was also investigated. Finally, the stability test of photocatalysts was carried out and the photocatalytic mechanism was explained concretely.

## 1. Introduction

Water pollutant has become a global issue of concern over the past few decades. The effluents have high content of organic pollutants, suspended solids (SSs) and fluctuating pH, making the conventional biological treatment method restricted [1,2]. Since Fujishima reported using $TiO_2$ electrode to generate oxygen and hydrogen under the irradiation of light in 1972 [3], photocatalysis was regarded as one of the most effective and economical ways to remove the organic pollutants from wastewater. In the past few years, $TiO_2$ as an N-type semiconductor, has been playing an important role in water treatment due to its advantages of attractive, enviromentally safe, low energy and non-toxicity [4]. The commercial P25 is a kind of $TiO_2$ powder which consists of 80% of the anatase phase and 20% of the rutile phase of $TiO_2$. These commercial titania nanoparticles have been widely used as photocatalysts in photochemical reactions due to their high photocatalytic activity. $TiO_2$ has a band-gap energy of 3.2 eV, when photon illuminates $TiO_2$ at proper energy ($\lambda < 400$ nm), it can excite electrons jumping from valence band to conductive band and generating electrons ($e^-$) and holes ($h^+$), these electron-hole pairs produce a series of oxidation-reduction reaction which can oxide organic pollutant into $CO_2$ and $H_2O$ [5–8]. Despite many benefits of using $TiO_2$ to treat water, there are some disadvantages that hinder commercialization. Due to the band-gap energy of $TiO_2$, it can just be activated by UV light of which the portion in sunlight is only 4–5%. Moreover, recombi-

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[*] Corresponding author at: Department of Chemistry, School of Science, Beijing Jiaotong University, Beijing, China.
*E-mail address:* wbduan@bjtu.edu.cn (W. Duan).

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nation of photo-generated electron-hole pairs also remains to be resolved [9,10]. Therefore, improving these weaknesses of $TiO_2$ is a critical need. The most feasible modification method seems to be doping with metals and non-metals.

The impurities induced by metal ions doping into the $TiO_2$ could efficiently narrow its band gap and extend the absorption edge into the visible light range. Many studies have demonstrated that metal ions doping could effectively improve the photocatalytic activity of $TiO_2$ under visible light irradiation [11–14]. In recent years, $TiO_2$-$In_2O_3$ composite photocatalysts have been attracted by many researchers. $In_2O_3$ with an indirect band gap of 2.8 eV had been proved to be an efficient sensitizer for photocatalysts to extend the absorption spectra from the UV region into the visible region [15]. There are some specific characteristics of indium, such as relatively cheaper, trapping and mobility, higher electron production and lower toxicity [16]. Thus, indium doped $TiO_2$ composite photocatalysts have been explored extensively including nanoparticles, films and so on. According to the precious work, Wang et al. [17] prepared indium doped $TiO_2$ by sol-gel method, which has revealed that the photo-generated carriers generated under visible light irradiation can be efficiently separated by the surface state energy level of the O-In-$Cl_x$ species and the valence band of $TiO_2$ contributing to enhance the photocatalytic activity. They also reported the amount of hydroxyl groups on $TiO_2$ surface increased greatly after being doped with indium. Jiang et al. [18] reported $TiO_2$-$In_2O_3$ nanocrystals heterojunction exhibited high photocatalytic activity for degradation of RhB, which was attributed to $In_2O_3$ leading to the interfacial transfer of photo-generated electrons and holes among $TiO_2$. Petronella et al. [19] showed $TiO_2$-$In_2O_3$ surface films enhanced effectively in bacterial inactivation under visible light because of their high surface area. Niyomkarn et al. [20] prepared mesoporous-assembled $TiO_2$-$In_2O_3$ mixed oxide photocatalysts. They were more responsive to visible light and more efficient in degradation of contaminant in aqueous solution due to its uniform pore size, high specific surface area and suitable crystallite size that can facilitate the electron and hole transportation for reacting with water or oxygen molecules adsorbed on its surface along the mesoporous-assembled structure to generate many active species. Nowotny et al. [21] had also discussed the electrical properties and defect of indium doped $TiO_2$.

Although the metal ion doping of $TiO_2$ has done great contributions to inprove photoactivity of catalysts under visible irradiation, the presence of metallic ions was also found to induce reduced thermostability of $TiO_2$ and to introduce additional recombination centers at increased doping levels [5]. It has been demonstrated extensively that anion doping, such as carbon, nitrogen and sulfur, was an effective approach to introduce visible light photocatalytic activity to $TiO_2$ since Asahi et al. [22] early reported nitrogen doped $TiO_2$. But as the precious work had proved, C-doped $TiO_2$ was more active than N-doped $TiO_2$ [23]. Using anodic oxidation method, Li et al. [24] successfully synthesized carbon modified $TiO_2$ nanotube exhibiting a great enhancement on visible light absorption. Teng et al. [25] fabricated carbon/$TiO_2$ nanocomposites by one-step carbonization method, the results suggested the prepared catalysts were affected severely by the state of carbon on the surface of $TiO_2$. Lin et al. [26] reported that C-doped mesoporous $TiO_2$ film was prepared by sol-gel process combining with hydrothermal treatment. The prepared C-doped $TiO_2$ film exhibited extraordinary photocatalytic activity in the degradation of dye Red X-3B, which resulted from the formation of O-Ti-C bonds. Zhang et al. [27] proposed that $TiO_2$/carbon core-shell nanocomposites fabricated via a two-step hydrothermal method significantly enhanced photocatalytic activity in the degradation of RhB, which may contribute to the high content of surface oxygen vacancies after the second hydrothermal treatment. Kamisaka et al. [28] have also attempted to analyze the structure and optical properties of carbon doped $TiO_2$ in theoretics.

Thus, it will be beneficial to use the synergetic effect of metal and non-metal ions doping like indium and carbon for enhancement of visible light response and photocatalytic activity. In the present study, different weight percentage of indium and carbon co-doped P25 nanocomposites were obtained by a thermal heating method. To the best of our knowledge, there has been no report on indium and carbon co-doped P25 as visible light photocatalyst. Hence both indium and carbon were selected for this co-doping work. In order to evaluate the performances of these co-doped catalysts soundly, they were employed as the photocatalysts to decolorize both cationic MB and anionic RR4 dye respectively under visible light irradiation. Moreover, as expected, they exhibited much better visible light photocatalytic activity than pure P25. Furthermore, the mechanism is discussed detailedly in this contribution for better understanding photocatalysis. Simultaneously, the effect of initial pH values on the photocatalytic degradation of MB and RR4 was also investigated below.

## 2. Experimental

### 2.1. Materials

All the reagents and chemicals were analytical grade and used without further purification. Commercial P25 was sourced from Sinopharm Chemical Reagent. Reactive Red 4 dye (RR4, chemical formula: $C_{32}H_{23}ClN_8Na_4O_{14}S_4$) and methylene blue (MB, chemical formula: $C_{16}H_{18}ClN_3S$) simulated as the organic pollutants were provided by Aladdin. Indium chloride and glucose purchased from Sinopharm Chemical Reagent were used as the precursors for indium and carbon respectively. Absolute ethanol and distilled water were used for the preparation of catalysts. Furthermore, hydrochloric acid and sodium hydroxide solution were used to adjust the initial pH values of organic dye solution in photocatalytic experiment. Table 1 provides a summary of organic pollutants models used in this work.

### 2.2. Methods

#### 2.2.1. Preparation of In/C-P25 composites

The modified catalysts were prepared by the following steps. 30 mL absolute ethanol and 20 mL distilled water were mixtured, labeled solution A. Added 2 g P25 into the solution A with stirring for 30 min to get a homogeneous suspension. And then 0.5 g glucose were added into the suspension. Afterwards, an appropriate amount of $InCl_3$ was dissolved into the mixture at room temperature. The mixture was stirred continuously and dried at 100 °C for 12 h in a ventilation oven. The dry solid sample was ground in an agate mortar, then calcined in the furnace. The furnace temperature was increased at a rate of 5 °C $min^{-1}$ until 400 °C, this temperature was held for 3 h. Finally, the In/C-P25 composite was obtained. The indium concentration in the catalysts was adjusted by changing the stoichiometric amount of $InCl_3$, while the carbon concentration was the same. The obtained samples were denoted as x% In/C-P25, where x% represented the nominal molar percentage of $In^{3+}$ ions in $Ti^{4+}$ and $In^{3+}$ ($In^{3+}/Ti^{4+} + In^{3+}$), and equaled to 5%, 10%, 15% and 20% respectively. For comparison, C-P25 and 15% $In_2O_3$-P25 samples were prepared as well with the same route, with and without the addition of the corresponding dopant.

#### 2.2.2. Chracterization

The crystal phase of materials were characterized by X-ray diffraction (XRD) and patterned a collection in a 2θ range from 10° to 80° using a RIGAKU Ru-200B diffract meter equipped with Cu Kα irradiation with a fixed power source (40 kV, 40 mA). The average crystallite size was determined from the broadening of the diffraction peak using the Scherrer formula