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

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Abstract

The commercially available TiO_2 Degussa P25 was modified using a simple technique to produce a visible-light-activated 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 photoelectron 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% $\text{In}_2\text{O}_3/\text{C-P25}$ showed the highest degradation rate of organic dye, which the removal efficiency can reach over 90% after 90 minutes and the corresponding hydrogen evolution rate of 15% $\text{In}_2\text{O}_3/\text{C-P25}$ 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% $\text{In}_2\text{O}_3/\text{C-P25}$ catalyst was also investigated. Finally, the stability test of photocatalysts was carried out and the photocatalytic mechanism was explained concretely.

Keywords

$\text{In}_2\text{O}_3/\text{C-P25}$; Synergistic effect; Visible light; Organic dye; Stability

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, environmentally 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 oxidize 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, recombination 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 improve 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 TiO₂/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 TiO₂ 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: C₃₂H₂₃ClN₈Na₄O₁₄S₄) and methylene blue (MB, chemical formula: C₁₆H₁₈ClN₃S) 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.

Table 1

Summary of organic pollutants.

Organic pollutants and chemical structures	Properties		
	Chemical formula	Mole mass (g mol ⁻¹)	Absorption max (nm)
<p>Methylene blue</p>	C ₁₆ H ₁₈ ClN ₃ S	319.85	664 nm
<p>Reactive Red 4</p>	C ₃₂ H ₂₃ ClN ₈ Na ₄ O ₁₄ S ₄	995.23	517 nm

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 mixed, 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 InCl₃ 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 InCl₃, 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 In³⁺ ions in Ti⁴⁺ and In³⁺ (In³⁺/Ti⁴⁺ + In³⁺), and equaled to 5%, 10%, 15% and 20% respectively. For comparison, C-P25

and 15% In₂O₃-P25 samples were prepared as well with the same route, with and without the addition of the corresponding dopant.

2.2.3. Characterization

The crystal phase of materials were characterized by X-ray diffraction (XRD) and patterned a collection in a 2 θ range from 10° to 80° using a RIGAKU Ru-200B diffract meter equipped with Cu K α 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 ($d = K\lambda / \beta \cos\theta$). Sample morphologies were observed by high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20) and field-emission scanning electron microscope (FE-SEM, Hitachi-S4800). The N₂ adsorption-desorption isotherms were measured using Micromeritics sorption analyzer (ASAP 2020). Prior to analysis, the samples were degassed for 6 h at 150°C under vacuum (10⁻⁵ mbar) in the degas port of the adsorption analyzer and the specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Chemical components of products were examined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). The UV-vis diffuse reflectance spectroscopy (DRS, Cary 5000) was used to measure the light absorption of the prepared photocatalysts, which was recorded in the range of 300-700 nm. The photoluminescence emission spectra (PL, FLS-980) of samples was tested to investigate the recombination of photogenerated electron-hole pairs. The samples were excited at 280 nm.

2.2.4. Photocatalytic degradation

The photocatalytic activity of different photocatalysts were evaluated by monitoring the degradation of cationic MB dye and anionic RR4 dye respectively. The experiments were carried out at room temperature in a photoreactor (XPA-7) with a 500 W xenon lamp as irradiation source which is surrounded by all cylindrical containers and placed 10 cm away from these containers. 50 mg of all prepared catalysts were suspended in 100 mL aqueous solution of organic dyes with the concentration of 30 mg L⁻¹ in a beaker. Prior to irradiation, the system was placed in a total dark environment under magnetic stirring for 30 min to investigate the adsorption behaviors of the photocatalysts. Following this, the photocatalytic reaction was started by the exposure of visible light. During the reaction process, vigorous agitation was performed in each container to guarantee the uniform irradiation of the photocatalysts. A certain organic dye solution was taken out at regular intervals of 15 min and analyzed after centrifugation followed by filtration to remove the catalyst particles. The degradation efficiency of pollutants was measured by detecting their absorbance at 664 nm for MB and 517 nm for RR4 using a UV-vis spectrophotometer. The photometric analysis of the all photocatalyst samples before and after irradiation can be used by measuring degradation efficiency of dye ($D\%$) defined by the following expression:

$$D\% = \frac{C_0' - C}{C_0'} \times 100\% \quad (1)$$

where C_0' is the initial concentration of MB and RR4 dye solution when the light turned on and C is the concentration of them after irradiation of the samples in desired time interval. All samples were tested under the same experimental conditions.

2.2.5. The stability test of photocatalysts

In order to evaluate the stability of the photocatalysts, a recycled usage experiment was carried out. 50 mg 15% In₂O₃/C-P25 photocatalyst was suspended in a 100 ml of 30 mg L⁻¹ solution of dye and irradiated under xenon lamp for 90 min. The samples were then centrifuged and the residues were collected, washed by distilled water and ethanol, then dried in the oven at 100°C. Finally, the photocatalyst was reused again for the second cycle of degradation with a fresh dye solution. This process was about to repeat up to 5 times of application.

2.2.6. Photoelectrochemical experiment

To determine the photoelectrochemical characteristic of all catalysts, the experiment of photocatalytic water splitting to generate hydrogen was carried out at ambient temperature and atmospheric pressure. Various of photocatalyst powders were fabricated via the procedure reported by Ito et al. [29] to produce electrodes. The experiment were processed in a quartz photoreactor where has three-electrode configuration using the P25 and the prepared photocatalysts as working electrode, a Pt wire as counter electrode and Ag/AgCl as reference electrode, which were immersed in the electrolyte containing 100 ml 20 vol% ethanol and distilled water mixed solution. Prior to irradiation, the suspension of the catalysts was dispersed by an ultrasonic clean for 10 min, and then the system was evacuated for 30 min to ensure the reactor was in an anaerobic condition. A xenon lamp located above the reactor was used as the light source. The generated gas was

collected by a probe in 20 min interval and analyzed using a gas chromatography (GC-14C) with N₂ as the carrier flowing at 20 ml L⁻¹. The photocatalytic activity of different samples was evaluated by the H₂ evolution rate in the same concentration range.

3. Results and Discussion

3.1. XRD Analysis

XRD patterns of pure P25, C-P25, 15% In₂O₃-P25 and 5%, 10%, 15%, 20% In₂O₃/C-P25 composites are shown in Fig.1, indicating that the diffraction peaks of all samples at 2θ values of 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.9°, 70.3° and 75.1° could be perfectly indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes of anatase TiO₂. Moreover, the patterns clearly show peaks of rutile TiO₂, namely, the planes (110), (101) and (111) at 2θ values of ca. 27.4°, 36.1°, 41.2° respectively. No diffraction patterns corresponding to In₂O₃ species were observed because of lower dopant concentration. Furthermore, there was also no phase transformation occurred for all carbon doped samples which were calcined at 400°C. According to Zhang et al. [30], they have observed the occurrence of phase transformation of carbon coated TiO₂ only when the calcining temperature was at 900°C. The diffraction peak of (101) planes was selected to estimate the crystallite size of all samples by the Debye-Scherrer equation:

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where *d* is the average thickness of the crystal in a direction normal to the diffracting plane (hkl), *β* is the crystallite size contribution to the peak width at half maximum intensity in radians and *K* is Scherrer constant. The crystallite sizes were 17.5, 18.2, 10.4, 18.0, 16.6, 12.8, 11.2 nm for pure P25, C-P25, 15% In₂O₃-P25, 5%, 10%, 15% and 20% In₂O₃/C-P25 respectively indicating that the introduced indium provided different boundaries and resulting in the inhibition of the growth of TiO₂ crystals [31]. The carbon doping on TiO₂ facilitated particles growth and increased the crystallite size. Meanwhile, compared with pure P25, the carbon doped sample had an increased intensity due to its higher crystallinity. Furthermore, increase in the indium dopants concentration showed decrease in crystallite size due to the strong inhibition imposed by indium doping on the growth of TiO₂ crystals. According to doping theory, it was documented that there are two kinds of doping modes, interstitial and substitutional for doped ions in oxides [32]. In the case of interstitial mode, the doped ions radius should be smaller than that of metal ions lattice, but for In³⁺ ions (0.081 nm) and Ti⁴⁺ ions radius (0.068 nm), the radius of In³⁺ ions is apparent larger than Ti⁴⁺ ions. Therefore, it is impossible for In³⁺ ions to enter into the crystal cell of TiO₂ through the interstitial mode. On the other hand, for the substitutional mode, when the radius of doping ions and lattice ions are close, lattice ions can be substituted by the doped ions in the oxide. If the ionic radius of the doping ions is larger than that of the lattice ions, the positions of all of the diffraction peaks in XRD patterns should shift to lower diffraction angles. As shown in Fig.1, there was slight shift of the diffraction peaks towards lower angles in XRD patterns of all indium doped samples. On the contrary, the diffraction peak at 25.3° moved towards the direction of higher angles for C-P25 samples. Since the ionic radius of Ti⁴⁺ (0.068 nm) and In³⁺ (0.081 nm) ions are close and Ti⁴⁺ can be substituted by In³⁺ ions. Meanwhile, the carbon ions with ionic radius of (0.016 nm) can be substituted for the lattice oxygen ions of ionic radius (0.140 nm). It is reasonable to suppose that indium and carbon ions are incorporated into the TiO₂ matrix for the substitution of indium and carbon for titanium and oxygen respectively in the TiO₂ lattice.

Fig. 1. XRD patterns of all samples.

3.2. N₂ Adsorption-Desorption Analysis

The textural properties of P25, C-P25, 15% In₂O₃-P25 and all In₂O₃/C-P25 samples were obtained from the N₂

adsorption-desorption analysis and the results were shown in Fig.2. It can be observed that all the isotherms belonged to type IV adsorption isotherm according to IUPAC classification and exhibited H3 hysteresis loop. This indicates that the powders had mesopores with narrow slit like shape [33]. Table 2 summarized the crystallite size and specific surface area of various samples. The specific surface areas of the photocatalysts varied in the range of 60-92 m²/g. Among all the prepared photocatalysts, BET surface area of 15% In₂O₃/C-P25 catalyst was found to be the maximum of 92 m²/g, which played an important role for the enhancement of photocatalytic activity. At higher dopant concentration, the well dispersed In₂O₃ species obstructed the pores and active sites of TiO₂, thus decreased the specific surface area [31].

Fig. 2. N₂ adsorption-desorption isotherms of P25, C-P25, 15% In₂O₃-P25 and In₂O₃/C-P25 samples.

Table 2

Textural properties of P25, C-P25, 15% In₂O₃-P25 and In₂O₃/C-P25 samples.

Catalysts	Crystallite size (nm)	Specific surface area (m ² /g)
P25	17.5	60
C-P25	18.2	73
15% In ₂ O ₃ -P25	10.4	78
5% In ₂ O ₃ /C-P25	18.0	82
10% In ₂ O ₃ /C-P25	16.6	85
15% In ₂ O ₃ /C-P25	12.8	92
20% In ₂ O ₃ /C-P25	11.2	89

3.3. XPS Analysis

The X-ray photoelectron spectroscopic analysis has been employed as an important characteristic method to detect the chemical states of different species in the doped TiO₂ samples. The XPS survey spectrum of 15%In/C-P25 catalyst shown in Fig.3a indicated that peaks corresponding to Ti, Cl, C and In elements. The high resolution XPS spectrum with scanning over the area corresponding to the binding energies for the Ti2p region was analyzed in Fig.3b. The representative Ti2p XPS spectrum indicated two peaks located at 458.9 eV and 464.5 eV were assigned to Ti2p_{3/2} and Ti2p_{1/2}, which agreed with the values of Ti⁴⁺ in tetragonal structure [34,35]. For the Cl2p XPS spectrum respresented in Fig.3c, the binding energy of Cl2p_{3/2} (198.8 eV) located between that of Cl2p_{3/2} in TiCl₄ (198.2 eV) and InCl₃ (199.1 eV) indicated to Cl2p_{3/2} in O-In-Cl_x (x=1or 2) species which was formed from the indium source. Since the radius of Cl⁻ ion is 0.181 nm, the the lattice O (0.132 nm) in TiO₂ can hardly be substituted by Cl⁻ ions. Thus, it can be concluded the formation of O-In-Cl_x structure is on the TiO₂ surface [17]. High resolution C1s spectrum can be observed was shown in Fig.3d and a broad energy range from 282 eV to 290 eV can be observed. The main peak was observed at 248.8 eV, which corresponded to the residual carbon from the organic precursor [36,37], while other weak peaks located at 286.7 eV and 288.9 eV were characteristics of the oxygen bound species C-O and C=O respectively [38,39]. The peak at 282.3 eV was close to the C1s peak (281.8 eV) of TiC. Accordingly, the C1s peaks at 282.3 eV can be ascribed to carbon substituting for the oxygen atom in the lattice of TiO₂, forming the O-Ti-C bond [40]. Therefore, it can be concluded that carbon has been successfully doped into P25. The XPS spectrum for In3d was revealed in Fig.3d, the double peaks centered at binding energies of 445.4 eV and 452.9 eV represented In3d_{5/2} and In3d_{3/2} which were assigned to In³⁺ species. Moreover, the binding energyof In3d_{5/2} in In/C-P25 (445.0 eV) located between that of In3d_{5/2} in In₂O₃ (444.6 eV) [41] and InCl₃ (446.0 eV) [42], also indicated In³⁺ ions were

linked with the unsaturated oxygen and Cl⁻ ions respectively. Compared with the reported In3d_{5/2} signal of metallic indium which appeared at 443.6 eV, the absence of this peak excluded the existence of metallic indium, suggesting the loaded indium existed in the oxide state [43,44]. The O1s core level peak at 530.3 eV (Fig.3f) could be ascribed to lattice oxygen in TiO₂ which also verified the existence of O-Ti-C and another peak at 532.1 eV associated to surface hydroxyl groups.

Fig. 3. (a) XPS survey spectra; High resolution XPS spectra of (b) Ti2p, (c) Cl2p, (d) C1s, (e) In3d and (f) O1s region of 15% In₂O₃/C-P25 samples.

3.4. Morphological and Structural properties

Morphological features of different samples were examined by field-emission scanning electron microscopy (FE-SEM) and the corresponding images were shown in Fig.4. From Fig.4a, it can be observed that P25 showed well dispersed spherical aggregated tiny particles of uniform diameter. Compared to P25, SEM images of doped samples depicted in Fig.4b and Fig.4c indicated that the spherical aggregates of particles exhibited varying sizes which was affected by the presence of indium and carbon. Furthermore, energy dispersive X-ray (EDX) spectra have also been carried out to determine the elemental compositions of doped catalysts. From Fig.3d, the elements of Ti, O and C were detected with random selection, which revealed P25 has been loaded with carbon. In the mean time, Ti, O, C, In and Cl peaks were obviously found in the spectra of Fig.4e, confirming the three components of In/C-P25 were assembled together. The EDX results showed the atomic percentages of Ti, O, C, In and Cl were 54.31%, 37.26%, 3.44%, 3.60% and 1.39% respectively. To further obtain the microscopic structure information, high resolution transmission electron microscopy (HRTEM) of different samples have been carried out, as displayed in Fig.5. The particles of all samples were roughly spherical in shape and the particle size distributed in the range of 10-20 nm. TEM images also confirmed that the average particle size of In₂O₃/C-P25 was more or less the same with P25 particles as can be seen in Fig.5a and Fig.5b. The clear lattice fringes of pure P25 and In/C-P25 catalysts were observed in the magnified HRTEM images which were shown in Fig.5c and Fig.5d. The pristine TiO₂ had layered structure with lattice spacing of 0.361 nm, which can be assigned to the (101) plane of anatase TiO₂. In Fig.5d, there was a slight increase about the fringe spacing for (101) crystallographic plane of TiO₂ from 0.361 nm to 0.368 nm. Therefore, it can be expected on substitution of dopant ions with larger ionic radius in the titania lattice [45], which can be consistent with the XRD results.

Fig. 4. FE-SEM images of (a) P25, (b) C-P25 and (c) 15% In₂O₃/C-P25; EDX of (d) C-P25, (e) 15% In₂O₃/C-P25.

Fig. 5. HRTEM images of (a) P25, (b) 15% In₂O₃/C-P25; Magnified image of (c) P25, (d) 15% In₂O₃/C-P25 sample.

3.5. Optical Properties

3.5.1. UV-vis DRS

As can be seen in the Fig.6a, the UV-vis diffuse reflectance spectroscopy of samples were observed. The absorption onset of pure P25 was about 388 nm. However, the doped composites cause a red shift in the absorption edge from 424 to 472 nm. The results indicated the light absorption range of doped catalysts were significantly shifted towards the visible light region comparing with the pure P25. It is generally presumed that the red shift is caused by the new impurity energy level in the band gap. The band gap energy can be calculated by Kubelka-Munk equation:

$$E_g = \frac{1240}{\lambda_g} \quad (3)$$

where λ_g is the absorption onset wavelength (nm) of the exciting light. The band gap energy values based on the onset of absorbance were found to be 3.19, 2.92, 2.89, 2.76, 2.71, 2.62 and 2.66 eV for P25, C-P25, 15% In₂O₃-P25, 5% In₂O₃/C-P25, 10% In₂O₃/C-P25, 15% In₂O₃/C-P25 and 20% In₂O₃/C-P25 samples respectively, which were consistent with the results of tauc plots shown in Fig.6b. According to other references, it could be explained that carbon doping promoted the formation of chemical bonds of O-Ti-C inducing localized occupied states into the band gap of TiO₂ lattice which narrowed the band energy of TiO₂ that rendered a red shift in the photo responding range and facilitated a more efficient utilization of light for the photocatalysis [46-48]. In addition, a wider range absorption in indium doped samples were attributed to the surface state energy level of the O-In-Cl_x (x=1 or 2) species which was located at 0.3 eV below the conduction band of TiO₂, which resulted in decreasing the bad gap energy of titania. Compared with the pristine and binary composites, it was noted that more increased absorption at the range of 400-700 nm for the In₂O₃/C-P25 samples. That was assigned to the synergistic effect of carbon and indium that facilitated the absorption of catalysts into visible region. Thus, it can be confirmed that doping metal ion such as indium and synergizing with carbon were efficient for visible light response and enhancing the photoactivity for the photocatalysts.

Fig. 6. (a) UV-vis diffuse reflectance spectroscopy, (b) tanc plots of transformed Kubelka-Munk functions of P25, C-P25, 15% In₂O₃-P25 and In₂O₃/C-P25 samples.

3.5.2. PL Emission

Photoluminescence (PL) emission spectra of all samples are shown in Fig.7. It is well known that PL spectra is to investigate the efficiency of charge transfer and electron-hole pairs separation. PL emission mainly depends on the recombination of electron-hole pairs. Lower emission intensity reveals the decrease of recombination rate, which is beneficial for improving the photocatalytic activity of catalysts. As can be seen in Fig.7, the peak positions of pure P25, C-P25 and $\text{In}_2\text{O}_3/\text{C-P25}$ were basically the same, representing the individual loading of indium and carbon has not induced new photoluminescence. Whereas, the peak intensity of all $\text{In}_2\text{O}_3/\text{C}$ co-doped P25 were significantly weaker than pure P25, which indicated the recombination of the photogenerated charge carriers were effectively inhibited. Further inspection of PL spectra revealed that 15% $\text{In}_2\text{O}_3/\text{C-P25}$ composite sample had the lowest PL intensity compared to other samples, which suggested that the recombination of photo-generated carriers were suppressed due to the cooperative effect of indium and carbon. This decrease in intensity as a result of decreased rate of electron-hole recombination facilitated the production of large number of $\cdot\text{OH}$ radicals, which enhanced the photocatalytic activity for degradation of pollutants [49]. However, indium also adversely worked as recombination centers when overloaded, reducing the suppression ability.

Fig. 7. Photoluminescence emission spectra of P25, C-P25 and $\text{In}_2\text{O}_3/\text{C-P25}$ samples.

3.6. Photocatalytic Activity

3.6.1. Degradation of organic dyes

The photocatalytic activities of P25, C-P25, $\text{In}_2\text{O}_3\text{-P25}$ and $\text{In}_2\text{O}_3/\text{C-P25}$ were evaluated by photo degradation of organic dyes (MB and RR4) which were acted as model contaminants under visible light. Fig.8 and Fig.9 presented the enhanced photocatalytic activities of doped catalysts with respect to that of pure P25. From the Fig.8a and Fig.9a, it can be seen that there was nearly no degradation of pollutants took place in the absence of photocatalysts under the visible irradiation after 90 min. Moreover, the degradation of MB and RR4 used by the all doped catalysts was always better as compared to the pristine P25 when both processes occurred simultaneously (adsorption and photocatalytic degradation). Among them, 15% $\text{In}_2\text{O}_3/\text{C-P25}$ showed the best photocatalytic performance, which both MB and RR4 were almost totally degraded. Further increase of indium doping did not enhance the photocatalytic activity of the catalyst. This may attribute to the fact that the surface area of the photocatalyst decreased with further increase of indium concentration [31] and the recombination of electrons and holes, which were detrimental to the photocatalytic activity of the catalyst. Fig.8b clearly showed the degradation efficiency of pure P25 was only about 36.2%. In addition, 15% $\text{In}_2\text{O}_3\text{-P25}$ and C-P25 were 65.2% and 58.7% respectively, which indicated 15% $\text{In}_2\text{O}_3\text{-P25}$ performed slightly better. However, the photocatalytic activity of 15% $\text{In}_2\text{O}_3/\text{C-P25}$ sample was topmost, which was about 92.8% of MB was decomposed after visible light irradiation for 90 min. It is about 2.6 times higher than the degradation rate of pristine P25. Similar observations were observed in Fig.9b that all catalysts were applied for the degradation of RR4 under visible light irradiation, the degradation rate of RR4 by using 15% $\text{In}_2\text{O}_3/\text{C-P25}$ was over 90% as well. The degradation efficiency of pure P25 was found to be the lowest among all catalysts due to the fact that pure P25 has the band energy of 3.2 eV, which is more active in UV region. Doping indium and carbon narrowed the band gap of TiO_2 , thereby enhancing the photocatalytic activity under visible light. The red shift in the light absorption towards visible region for indium and carbon co-doped P25 has also been proved in UV-vis DRS results. In conclusion, the photocatalytic activity is in the order of 15% $\text{In}_2\text{O}_3/\text{C-P25}$ > 10% $\text{In}_2\text{O}_3/\text{C-P25}$ > 20% $\text{In}_2\text{O}_3/\text{C-P25}$ > 5% $\text{In}_2\text{O}_3/\text{C-P25}$ > 15% $\text{In}_2\text{O}_3\text{-P25}$ > C-P25 > P25. According to these results, it can be concluded that doping indium and carbon can be considered as an effective way to improve photoactivity for preparing TiO_2 -based photocatalysts. In addition, the photocatalytic mechanism will be demonstrated concretely in the following section.

Fig. 8. (a) Photodegradation of MB over all photocatalysts; (b) Photocatalytic degradation rate of photocatalysts.

Fig. 9. (a) Photodegradation of RR4 over all photocatalysts; (b) Photocatalytic degradation rate of photocatalysts.

3.6.2. Kinetics Analysis

The kinetics study of photocatalytic degradation of MB was discussed using kinetic model proposed by Langmuir-Hinshelwood [50,51] according to the equation as follows:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (4)$$

where C is the concentration of MB at time and C_0 is the initial concentrate of MB when the light was turned on, k is a rate constant and t is time. From the Fig.10, the linear relationship between $\ln(C/C_0)$ and irradiation time was observed, which suggested that the degradation of MB obeyed the first order reaction kinetics. The degradation of the MB with average rate constants for P25, C-P25 and 15% In_2O_3 /C-P25 were 4.9×10^{-3} , 9.4×10^{-3} and $2.91 \times 10^{-2} \text{ min}^{-1}$ separately. The rate constant for the C-P25 and 15% In_2O_3 /C-P25 were found to be about 2 and 6 times higher respectively in comparison to pure P25. Therefore, it can be revealed that the degradation efficiency of 15% In_2O_3 /C-P25 is the fastest.

Fig. 10. First order kinetics for MB in presence of various photocatalysts.

3.6.3. Effects of pH Values

pH values are not only an important factor influencing the degradation efficiency of organic compounds in the photocatalytic process but also vital variables in actual treatment of wastewater. Hence, extra experiments were carried out to determine the effect of pH values of organic dye solution. Using HCl or NaOH solution adjusted the solution at pH 3 and

12 respectively. Fig.11 illustrated that the 15% $\text{In}_2\text{O}_3/\text{C-P25}$ degradation efficiency of MB on condition that different pH values. It has been observed that both the adsorption behaviour and the photo-degradation rate of MB increased with increasing pH. The removal of MB can reach up to 96.1% at pH 12. The isoelectric point of 15% $\text{In}_2\text{O}_3/\text{C-P25}$ is 5.6 pH units based on our measurement, resulting in the surface of the catalyst having a negative potential in the range of $\text{pH} > 6$ [52]. Since MB is a cationic dye, there would be a greater probability to adsorb onto the surface of the catalysts to promote photocatalytic reaction at higher pH value. Another possible reason for the behavior as seen in Fig. 11 is that there are more hydroxide ions (OH^-) in alkaline condition that can react with the photo-generated holes to favor the formation of more hydroxyl radicals ($\cdot\text{OH}$), which could significantly enhance the photocatalytic degradation of the dye [53]. On the contrary, it is well known that RR4 is anionic dye. Based on the theory we have mentioned above, the opposite results presented in anionic RR4 experiment were as expected in Fig.12. With the increase of pH values from 3 to 12, the adsorption behaviour of 15% $\text{In}_2\text{O}_3/\text{C-P25}$ dropped. In addition, the highest degradation efficiency (94.9%) of RR4 was obtained in the solution of pH 3 and the lowest efficiency (88.1%) at pH 12 after 90 min irradiation. Thus it can be suggested that the influence of pH on photocatalysis is because of the amount of dye adsorbed on catalysts, and the degradation takes place at or near to the catalyst surface, rather than in the bulk solution.

Fig. 11. Effects of pH values on the degradation of MB by 15% $\text{In}_2\text{O}_3/\text{C-P25}$ samples.

Fig. 12. Effects of pH values on the degradation of RR4 by 15% $\text{In}_2\text{O}_3/\text{C-P25}$ samples.

3.6.4. Photoelectrochemical experiment

Since the as-prepared photocatalysts showed the perfect performance in the degradation of dye, hydrogen evolution experiment was further carried out to investigate the accurate photoelectrochemical property of the as-prepared samples. Before the actual photoelectrochemical experiment was started, pure ethanol solution was taken for the control experiment in the absence of either photocatalyst or irradiation. There was no hydrogen production observed in this experiment. The results excluded other influences of hydrogen generation except from the photocatalytic activities of as-prepared catalysts. Fig.13 showed the H_2 evolution of all catalysts as a function of irradiation time. As the time went on, the generation of hydrogen of all samples ascended steadily. Besides the photo degradation of MB, the pristine P25 presented the lowest photocatalytic efficiency in water splitting among all catalysts as well, which was only $0.273 \text{ mmol g}^{-1}$ after 5 h under visible light irradiation. Moreover, C-P25 performed much better than pure P25, which was $1.294 \text{ mmol g}^{-1}$. It can be concluded that the decrease of the band gap of P25 occurred with the carbon introduction which had been discussed above. As expected, the H_2 evolution rate of all the co-doped catalysts were up to 1.537, 1.912, 2.442 and $2.137 \text{ mmol g}^{-1}$ for the catalysts P25, C-P25, 5%, 10%, 15% and 20% $\text{In}_2\text{O}_3/\text{C-P25}$ respectively, which showed higher activity than C-P25. Among them, 15% $\text{In}_2\text{O}_3/\text{C-P25}$ showed the best photoactivity under the same condition. This was due to the synergistic effects of indium and carbon with the same reason of degradation experiment. Just as we mentioned in photoluminescence emission section, overloaded indium produced an adverse effect on the photocatalytic efficiency, which suggested that the photo-generated electrons recombination should be considered when increase the concentration of dopants.

Fig. 13. Visible-light-driven photocatalytic H₂ evolution over all photocatalysts.

3.6.5. The stability of photocatalyst

The stability is an important factor for catalysts. Cyclic photocatalytic degradation of organic dye solution was processed to detect the photocatalytic stability of P25 and 15% In₂O₃/C-P25. Every cycle experiment was conducted under the same condition. As shown in Fig.14, decoloration efficiency decreased gradually for both samples after several recycles because active sites on the surface of the samples may be covered by organic substances. Also, some small particles of the catalyst would be lost after washing and filtration in each cycle. However, the 15% In₂O₃/C-P25 presented much improved activity than P25 in each cycle and the decoloration efficiency decreased only about 2% after five circulations. By comparison, decoloration rate of P25 dropped from 36.2% to 14.9%, which represented an obvious decline. The similar results can be also seen in the RR4 experiment. Thus, it is no doubt to say that during the photocatalytic process, In₂O₃/C-P25 has superior sustainability and stability than the commercial P25. The stability of 15% In₂O₃/C-P25 was higher than on P25 mainly due to the enhanced surface area. The larger surface was allowed organic molecules more easily to access the active sites to participate the photocatalytic reaction. In addition, the adsorption of organic dyes on 15% In₂O₃/C-P25 was increased due to the charge imbalance on the TiO₂ surface where it was produced by -Ti-O-In-O-Ti- framework resulting from the substitution of In³⁺ in the titania lattice. This kind of chemisorption on the surface of TiO₂ was not easily removed even after 5 times of repeated usage.

Fig. 14. Photocatalytic efficiency of P25 and 15% In₂O₃/C-P25 upon recycled applications in the degradation of MB and RR4.

3.7. Photocatalytic mechanism

The photocatalytic mechanism of In₂O₃/C-P25 is illustrated comprehensively in this section. When the photocatalyst is irradiated by visible light, electron-hole pairs could be generated, then they react with water and dioxygen absorbed on the photocatalyst surface leading to more oxidized species to form hydroxyl radicals (•OH) and super-oxide radical anions (O₂⁻), these oxy radicals can attack organic compounds including MB and RR4, then decompose them into CO₂ and H₂O. The specific mechanism of photocatalysis mainly includes the following reactions:

This enhanced photocatalytic activity of multi-doped P25 arises due to the synergistic effect of dopants contribution to improve visible light absorption and increase of the lifetime of photo-generated charge carriers. Plausible mechanism for

the photocatalytic degradation of dye on $\text{In}_2\text{O}_3/\text{C-P25}$ nanocomposite was illustrated in Fig.15. It is well known that the doping of indium and carbon on TiO_2 plays a vital role in shifting the light absorption edge to visible region [54-56]. The prepared samples could activate the visible light, thus more electrons and holes would be generated and participated in the photocatalytic redox reactions. Doping of indium ions resulted in the formation of surface state energy level which was originated from the O-In-Cl_x species and 0.3 eV below the conduction band of TiO_2 . As a result, the band gap energy was reduced by indium doping. Carbon doping also led to the formation of the oxygen vacancies [57] and a new substitution of Cls band above O2p valence band. The substituted carbon introduced additional energy levels above the valence band [58]. After the co-doping with indium and carbon, the band gap could be narrowed due to surface state energy level formed below the conduction band of TiO_2 by the indium doping and the additional energy levels formed above the valence band because of the carbon doping. Therefore, electrons could be excited simultaneously from the additional energy levels to conduction band of TiO_2 (process ②) and the surface state energy level of O-In-Cl_x (process ③, ④) under visible light irradiation, which performed a higher absorption in visible light region as shown in Fig.6. Meanwhile, the photo-generated electrons at the conduction band can transfer to the surface state energy level of O-In-Cl_x (process ④) which locates higher than the energy levels of the oxygen vacancies (0.51 eV below conduction band) [60] and the photo-generated holes at valence band would transfer to the surface. As a result, the photo-generated electrons and holes can be separated efficiently on surface of $\text{In}_2\text{O}_3/\text{C-P25}$ sample, as confirmed by the photoluminescence measurement as shown in Fig.7, and then take part in the photocatalytic reaction. The doping of indium ions was also beneficial for accelerating the associated transfer of photo-generated electrons to the adsorbed O_2 molecules, thus efficiently extending the life time of electron-hole pairs [51,61]. Based on previous discussion, indium doping also promoted the adsorption of H_3O^+ and hence introduced the Brønsted acidity [62]. Thus, the absorbed OH^- groups on the TiO_2 surface were enhanced to form more hydroxyl radicals, which was beneficial for photoactivity of the catalyst. The co-doped P25 catalysts with indium and carbon can result in the formation of more structural defects, especially surface defects on photocatalysts [63], which increase the specific surface area of catalysts as shown in Table 2. This would improve the chemical adsorption capability of catalysts for organic molecules. Thus, it may contribute to the improved photocatalytic activity as well.

Fig. 15. Photocatalytic mechanism of $\text{In}_2\text{O}_3/\text{C-P25}$ composite.

4. Conclusions

In summary, $\text{In}_2\text{O}_3/\text{C-P25}$ co-doped photocatalysts were prepared by thermal heating method. The indium and carbon co-doped composites showed better photocatalytic activity than degussa P25 and carbon doped P25. Among all the synthesized photocatalysts with different dopant concentration, 15% $\text{In}_2\text{O}_3/\text{C-P25}$ had the highest photocatalytic activity in the degradation of MB and RR4 and the corresponding hydrogen evolution rate under visible light irradiation. The enhanced photocatalytic activity may be attributed to the following reasons: firstly, the band gap energy was reduced by the formation of additional energy level above the valence band by carbon doping and the surface state energy level below the conduction band of TiO_2 due to indium doping; secondly, doping of indium and carbon can inhibit the recombination of excitons and hence the life time of electron-hole pairs were efficiently extended; thirdly, indium doping introduced the Brønsted acidity which could form more hydroxyl radicals and these groups played an important role in degradation of organic pollutants. Therefore, it can be concluded that doping indium ion and synergizing with carbon on TiO_2 should be beneficial for the development of the TiO_2 -based photocatalysts with better performance under visible light irradiation. The

influence of pH values on the photocatalytic performance of 15% $\text{In}_2\text{O}_3/\text{C-P25}$ was also determined in extra experiment and the result manifested that the highest degradation of MB was at pH 12 while RR4 was at pH 3. In the end, according to the stability test, it can be suggested that $\text{In}_2\text{O}_3/\text{C-P25}$ composite was very stable and possessed excellent sustainability for the photocatalytic activity. We expected our work could give a new way of thought on exploration of TiO_2 photocatalysts.

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Graphical Abstract

Photocatalytic mechanism of In₂O₃/C-P25 composite.