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Correlation of fluorescence and photocatalytic activity of Co-doped TiO_2

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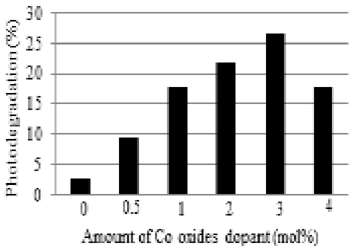
GRAPHICAL ABSTRACT



ABSTRACT

Co-doped TiO_2 (0.5-4 mol%) photocatalysts were synthesized via sol-gel method and their physical and chemical properties were investigated. Addition of Co oxide dopant induced anatase to rutile phase transition and reduced the band gap energy of TiO_2. The fluorescence result indicated that the electron-hole recombination rate was reduced with the presence of Co oxide dopant. The best photocatalyst obtained was 3Co-TiO_2 which enhanced the photocatalytic activity of TiO_2 by 12 folds to 26.6%. The importance of fluorescence properties of Co-doped TiO_2 towards its photodegradation of Congo Red was presented.

Keywords: fluorescence, photocatalysis, Co-doped titania

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1. INTRODUCTION

Water pollutant is predicted since approximately 1-15% of the synthetic textile dyes is lost in wastewater streams during manufacturing operations [1]. Hence, it is crucial to treat the wastewater before it is drained to the river and sea. Congo Red (CR) is the first synthetic azo dye and it is widely used in cotton, textile, paper, rubber dyeing industries [2]. CR consists of benzidine structure which is possible to split into carcinogenic amines [3], but it is still widely used in dyeing industry due to its effectiveness and less costly. Hence, removing of CR is an important issue.

Photocatalysis appears to be environmental friendly method since it has the potential to utilize free solar light, operate at room temperature and does not generate secondary pollution compare to other conventional dye removal method including adsorption, filtration, oxidation etc. Metal oxide especially transition metal oxide have been widely attempted to improve the photocatalytic activity of TiO_2 under visible light irradiation [4]. Co oxide have been used to improve the photocatalytic activity of TiO_2 by various researchers [5, 6].

In the previous paper [7], we have demonstrated that Co-doped TiO_2 enhanced the photodegradation of Congo Red. It has been proposed that presence of Co^{3+} might play the role in capturing the electron leading to reduced electron-hole recombination rate. In the current study, additional characterization results were presented and highlighted the correlation between fluorescent study and the photodegradation of CR.

2. EXPERIMENTS

2.1 Photocatalyst Preparation

The method to synthesize 0.5 to 4 mol% Co-doped TiO_2 had been reported [7]. In a typical synthesis, pre-calculated cobalt (II) acetylacetonate (99%, Acros) dissolved in acetylacetone (≥ 99%, Aldrich) was added dropwise to titanium oxide (TiO_2) precursor which was prepared by mixing titanium tetraisopropoxide (97%, Aldrich), ethanol (99.98%, HmBG) and acetylacetone in the molar ratio 1: 100:2. The mixture was subjected for stirring at room temperature for 30 minutes, followed by evaporation and drying and calcination at 500 ˚C for 5 hours.

2.2. Characterization

The crystalline structure of the catalyst was determined with X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Kα radiation source in the range of 2θ = 20-80° with scan rate of 0.1°/s. The rutile phase was calculated using Spurr equation as shown in equation (1).

$$R(\%) = 100/(1+0.8[I_A/I_R]) \quad (1),$$

where I_A and I_R are the intensity values of the anatase at 2θ = 25.3° (101) and rutile peak at 2θ = 27.5° (110). Diffuse reflectance UV-Visible spectra of samples were recorded on Perkin Elmer Lambda 900 Ultraviolet-visible spectrometer with $BaSO_4$ as reference. Band gap energy was obtained from Tauc plot which is the plot of $(\alpha h\nu)^2$ against $h\nu$ where α is the absorbance obtained from diffuse reflectance UV-Vis spectrum, h is the Planck constant and ν is the frequency of light. $h\nu$ can be calculated as 1240/wavelength. The band gap value was determined by extrapolating the vertical segment of the plot to intersect on the x-axis when y-axis is zero. The fluorescence spectra of the photocatalysts (2.000 ± 0.005 g) were recorded by a spectrofluorometer (JASCO, FP-8500) with an excitation wavelength at 216 nm.

The photocatalytic activity of the samples was tested via photodegradation of CR under visible light irradiation using halogen fiber optic light illuminator (Dolan-Jenner MI 157, 150 W). UV longpass filter (400 nm, Edmund Optics) was used to allow only visible light (λ > 400nm) irradiated on the dye solution. Sample (0.1 g) was put into the beaker consisted of 50 mL 100 ppm of CR and subjected to light illumination for 24 hours. Adsorption test was carried out prior to photocatalytic study to ensure equilibrium has been achieved. After the photocatalytic reaction, the solution was centrifuged and the supernatant was withdrawn. The concentration of CR was determined using UV-Vis spectrometer (Thermo Fisher, Genesys 10S) at λ = 499 nm. The photocatalytic activity was examined by determining the decolorization percentage of $(C_o-C)/C_o$ of CR where C_o and C were the concentration of CR before and after the photocatalytic reaction, respectively.

3. RESULTS AND DISCUSSION

The ability of cobalt oxide dopant to induce anatase to rutile phase transformation was investigated and the XRD pattern is depicted in Figure 1. The percentage of antase and rutile phase is shown in Table 1. It was found out that it required up to 4 mol% Co oxide dopant to induced anatase to rutile phase transformation. The ionic size difference between Ti^{4+} (0.605 Å) and Co^{2+} (0.65 Å), and Co^{3+} (0.545 Å) is less than 15%, thus substitution of Ti^{4+} with either Co^{2+} or Co^{3+} is possible which lead to anatase to rutile phase transformation [8]. The added Co oxide could have initially incorporated in the interstitial position of TiO_2 framework when the amount of Co oxide was lower than 4 mol% and the additional Co oxide dopant could have incorporated inside TiO_2 framework in the substitutional position when 4 mol% Co oxide were doped. The crystallite size was calculated using Scherrer equation. Obviously, crystallite size of TiO_2 was reduced from 20.10 to 15.76 Å when doped with 0.5 mol% of Co oxide dopant. This indicated that Co oxide could inhibit the crystal growth of TiO_2. Further addition of Co oxide has negligible effect on the crystallite size of TiO_2.

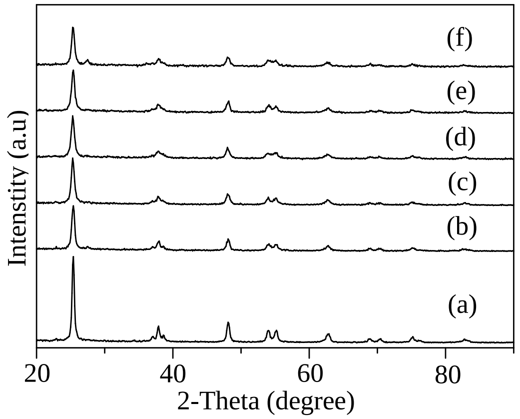

Fig. 1 XRD pattern of (a) TiO_2, (b) 0.5Co-TiO_2, (c) 1Co-TiO_2, (d) 2Co-TiO_2, (e) 3Co-TiO_2, (f) 4Co-TiO_2

Band gap energy is a crucial factor which determines if the sample is visible-light-driven photocatalyst. The band gap energies of the samples are shown in Table 1. Band gap energy of TiO_2 was successfully reduced by 42% from 3.25 to 2.35 eV when doped with 4 mol% Co oxide, indicating that the optical properties of TiO_2 has been successfully changed from UV active to visible light active with Co oxide doping. Since the standard reduction potential of Co^{2+}/Co^{3+} redox couple is 1.92 eV [9], the added Co oxide dopant can create additional energy level below the conduction band of TiO_2. In addition, when the amount of Co oxide dopant increase, the density of state of the dopant increase and form a continuum of states just like the bands and effectively the band gap energy decreased.

The fate of electron and hole recombination rate was studied via fluorescence analysis. The fluorescence spectra of TiO_2 and Co-doped TiO_2 are illustrated in Figure 2. The undoped TiO_2 and all Co-doped TiO_2 samples have similar emission spectra. Three peaks at 407, 467, and 553 nm were detected for all the samples. The first peak was corresponded to emission of band gap transition while the other two peaks were attributed to charge-transfer of oxygen vacancy trapped electron [10]. As can be seen, the peak intensity of TiO_2 reduced significantly after addition of 0.5 mol% Co oxide dopant. The peak intensity continually decreased with further increment of Co oxide dopant up to 3 mol%. Since the fluorescence emission is the result of recombination of excited electrons and holes, the lower emission intensity of the Co-doped TiO_2 inferred to a lower recombination rate. In other words, 3Co-TiO_2 has the lowest electrons and holes recombination rate among the prepared Co-doped TiO_2 samples.

Table 1 Rutile phase, crystallite size, band gap energy, surface area and adsorption ability of samples

Sample	**Rutile phase (%)**	**Crystallite size (nm)**	**Band gap energy (eV)**	**Adsorption (%)**
TiO_2	0	20.10	3.25	0.9
0.5Co-TiO_2	0	15.76	3.20	4.4
1Co-TiO_2	0	15.54	3.15	4.9
2Co-TiO_2	0	14.58	2.85	9.9
3Co-TiO_2	0	15.19	2.55	10.4
4Co-TiO_2	22	15.45	2.35	11.5

The reduced recombination rate could be attributed to the presence of Co^{3+}/Co^{2+} redox couple [11]. On the other hand, it was found that further loading of Co oxide into/onto TiO_2 has caused increment in peak intensity in the emission spectrum as evidenced in 4Co-TiO_2 sample. The finding may imply that 4 mol% Co oxide dopant was in excess and hence they acted as the recombination centre. As a result, the electron and hole recombination rate of 4Co-TiO_2 was slightly higher than that of 3Co-TiO_2. Furthermore, it was reported that rutile phase has more defect and hence led to greater electron-hole recombination rate [12].

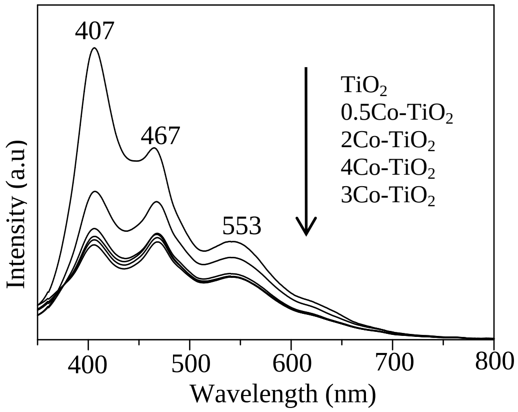

Fig. 2 Fluorescence spectra of TiO_2 and Co-doped TiO_2 samples

The photodegradation of 50 mL 100 ppm CR was tested over the prepared Co-doped TiO_2. Adsorption test was carried out in the dark before the reaction was carried out under visible light illumination. Results (Table 1) showed that the adsorption of dye on the photocatalysts increased with increasing of Co oxide dopant amount. After 2 hours, 4.4, 4.9, 9.9, 10.4 and 11.5% of CR were adsorbed on 0.5Co-TiO_2, 1Co-TiO_2, 2Co-TiO_2, 3Co-TiO_2, and 4Co-TiO_2, respectively. This phenomenon can be visualized by increasing of electrostatic charge interaction between cationic charge of Co ions on Co-doped TiO_2 samples and anionic charge of CR.

The results of photodegradation of CR are shown in Figure 3. It was demonstrated that addition of Co oxide enhanced remarkably the photocatalytic activity of TiO_2. The loading of cobalt oxide into/onto TiO_2 has gradually increased the photodegradation activity of CR, from 2.3% by undoped TiO_2 up to 26.6% by 3Co-TiO_2 photocatalyst. The increment was about 12 folds. The enhancement of the photocatalytic activity could be due to extension of absorption edge of TiO_2 to the visible light region which enabled utilization of visible light as activation source. In addition, the increment of electrostatic interaction between CR and Co-doped TiO_2 photocatalyst could also improve photocatalytic activity since photocatalysis is a surface reaction and the targeted pollutant must contact with the photocatalyst first for the degradation process to take place. The reduction of electrons and holes recombination rate as a result of the presence of Co^{3+}/Co^{2+} redox couple also led to the enhanced photodegradation of CR. Rather than extended absorption in visible region and reduced band gap energy, our research findings suggested that low electrons and holes recombination rate was the key factor for high photocatalytic activity. Amount of 3 mol% was the optimum Co oxide dopant amount to enhance the photodegradation of CR due to its lowest electrons and holes recombination rate. On the other hand, excess of Co oxide dopant in 4Co-TiO_2 hampered the activity due to over dosage. It was believed that the excess Co oxide acted as electrons and holes recombination center.

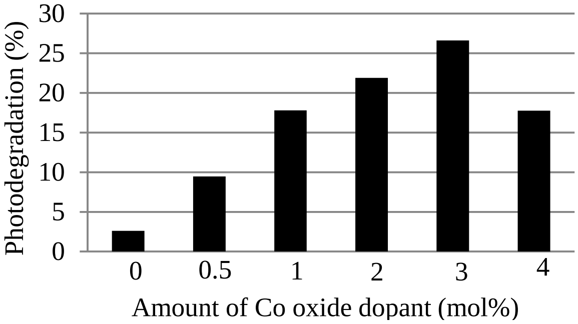

Fig. 3 Photodegradation of Congo Red by 0.5 to 4 mol% Co-doped TiO_2. (concentration of CR = 100 ppm, time= 24 hours, room temperature)

4. CONCLUSION

The current study indicated that the variation photodegradation of CR by Co-doped TiO_2 as a function of amount of Co oxide was closely related to the electron-hole recombination rate. Factors including presence of rutile phase, crystallite size, band gap energy and adsorption ability did not affect directly the photocatalytic behavior of Co-doped TiO_2 photocatalyst under visible light irradiation.

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