VISIBLE LIGHT DRIVEN CATALYTIC ACTIVITY OF CO-PRECIPITATED CO-DOPED TiO_2 PHOTOCATALYST

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Abstract

Co-doped TiO_2 nanopowders utilized as photocatalysts were successfully synthesized by co-precipitation method with various Co contents from 0-5 mol% using tetrabutyl titanate and Cobalt (II) nitrate hexahydrate as starting precursors for Ti and Co sources, respectively. Calcination process was conducted in order to improve crystallinity of the powders. The crystal structure and phase formation of both as-precipitated and after-calcined powders were characterized by X-ray diffraction (XRD) while morphologies of the powders were monitored by scanning electron microscope (SEM). Their optical absorptivity and corresponding band gaps were evaluated by diffuse reflectance spectroscopy. The photocatalytic activity of Co-doped TiO_2 photocatalysts against aqueous organic dye under visible light were carried out. The influences of Co-dopant and calcination temperature on photocatalytic performance of the catalysts were investigated. It is notified that incorporation of certain content of Co dopant into TiO_2 exhibits significant enhancement in its photocatalytic activity under visible light due to extended absorptivity into visible region of the powders with doping.

Keywords: Co-doped TiO_2, Co-precipitate process, Photocatalyst

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Introduction

Water pollution has been considered as an urgent environment issue in recent years. Photocatalytic metal oxide semiconductor nanoparticles such as TiO_2, SnO_2, and ZnO have attracted a great deal of attention in terms of their potential applications in photodegradation of pollutant in the environment. Among these semiconductors, titanium dioxide is considered as one of the most important materials due to its outstanding properties including a wide direct optical band gab energy (3.2 eV for anatase and 3.02 eV for rutile), chemical stability, environmental friendly and low-cost (Jiravat *et al.* 2013). Primarily, TiO_2 has three polymorphs including anatase, rutile and brookite. Typically, anatase phase of TiO_2 exhibits high photocatalytic activity for pollutant degradation comparing with other phases. Typically, anatase TiO_2 has characteristic absorption in UV region due to its wide band gap therefore photocatalytic reaction is unable to proceed under solar irradiation. High recombination rate of electron-hole pair is additionally recognized as a major limitation of TiO_2 photocatalyst (Liu *et al*., 2015 and Jun Dai *et al.,* 2015). Many methods have been alternatively proposed to improve its photocatalytic activity under visible irradiation. Doping method has been considered as an effective route to enhance its optical properties and photocatalytic performance. Metal dopants, such as Ag, Cu, Pt and Co, have been proven as proper incorporated element that can increase the photocatalytic ability of TiO_2 under visible irradiation (Liwei *et al*. 2012). Among these elements, Co ion incorporated into TiO_2 matrix could provide additional energy levels within the band gap of TiO_2 at which electron can consequently transfer to the conduction band using lower photon energy and electron-hole recombination may be reduced. This research work reports on the photocatalytic activity of co-precipitated Co-doped TiO_2 under visible irradiation with various Co contents from 0-5 mol%. Anatase Co-doped TiO_2 and calcined at 400 °C was characterized by X-ray diffraction. The morphologies of the samples were monitored by scanning electron microscope. Their optical absorptivity and corresponding band gaps were evaluated by reflectance spectroscopy. The photocatalytic activity of Co-doped TiO_2 against aqueous organic dye RhB under visible light was carried out and compared to that of commercial Degussa P25.

Meterials and Methods

Sample Preparation

Co-doped TiO_2 photocatalysts were synthesized by co-precipitation method with various cobalt dopants 0-5 mol% using titanium (IV) isopropoxide and cobalt (II) nitrate hexahydrate as starting precursors. Each precursor was dissolved in absolute ethanol under vigorous stirring at room temperature for 20 min. Subsequently, both solutions were mixed together. Ammonium (NH_3) acting as precipitation agent was slowly added drop-wise into the mixed solution until pH reached 9 under vigorous stirring. The obtained precipitate was stirred continuously for 3 h and was aged for 24 h at room temperature. As-synthesized precipitates were acquired by washing several times with distilled water in order to remove residual and unwanted impurities until pH became neutral. As-synthesized precipitate of Co-doped TiO_2 catalyst was dried at 100°C for 24 h. The anatase phase of Co-doped TiO_2 catalysts were obtained by calcined at 500°C with heating rate of 5°C/min for 3 h.

Characterization

The crystallinity of the catalysts was investigated using X-ray diffraction (XRD; PANalytical X'Pe°Pro) operating with copper radiation (Cu-K_α; λ=0.154 nm) at a generator voltage of 40 kV and a current 30 mA. The data were recorded in the 2θ range of 20° to 80° with a scanning rate of 0.02° s^{-1}. The morphologies of the catalysts were observed by scanning electron microscope (SEM; EVO MA10). Their optical absorptivity was evaluated by reflectance spectroscopy (UV-Vis DRS; Shimadzu UV-3600) in a wavelength of 200-1200 nm. Before UV-Vis measurement, 0.4 g of samples was pressed into a circular pellet of

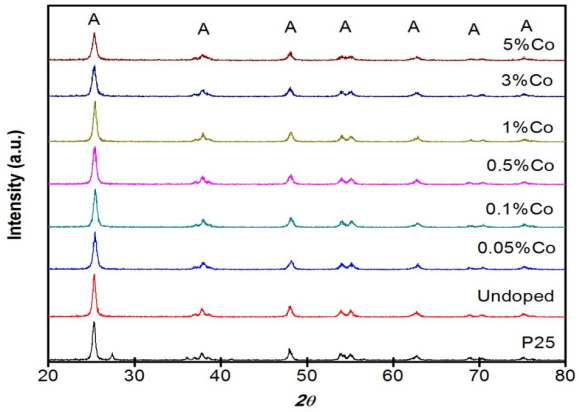

Figure 1. XRD patterns of commercial Degussa P25 and calcined Co-doped TiO_2 with various Co doping contents at 0-5 mol% catalyst

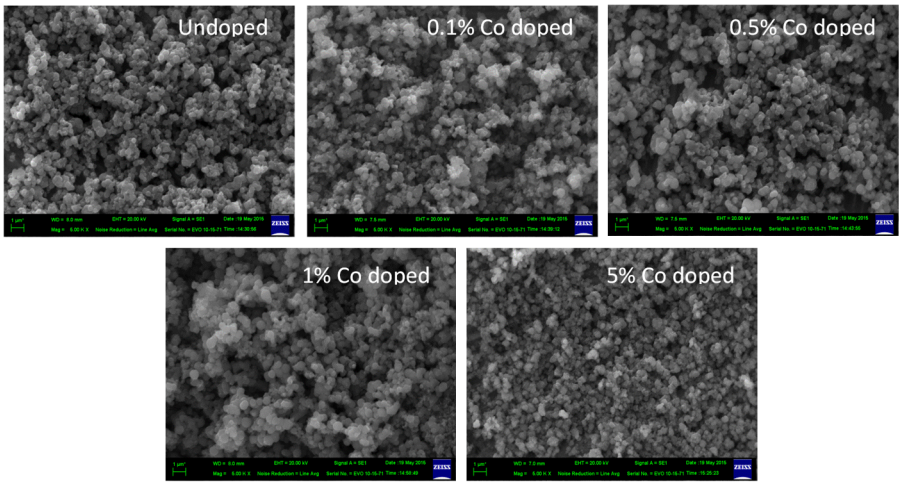

Figure 2. SEM images of calcined Co-doped TiO_2 with various Co doping contents at 0-5 mol% catalyst

1.2 mm in diameter under 2.5 ton pressures for 2 min by hydraulic pelletizer. The corresponding optical band gap values are estimated upon the Kubelka Munk Method combined with the Tauc relation.

Photocatalytic Activity

The photocatalytic activities were evaluated by dye photodegradation of Rhodamine B (RhB) under the irradiation of 700 W of white light emitting diode (LED). 50 mg of the catalyst was dispersed into 100 ml of RhB with concentration of 1 mM. Prior to the irradiation, the mixture was stirred for 3 h in the dark to obtain the formation of homogeneous suspension and absorption/desorption equilibrium between RhB and catalyst surfaces (Wanichaya *et al.* 2011). The solution was irradiated under

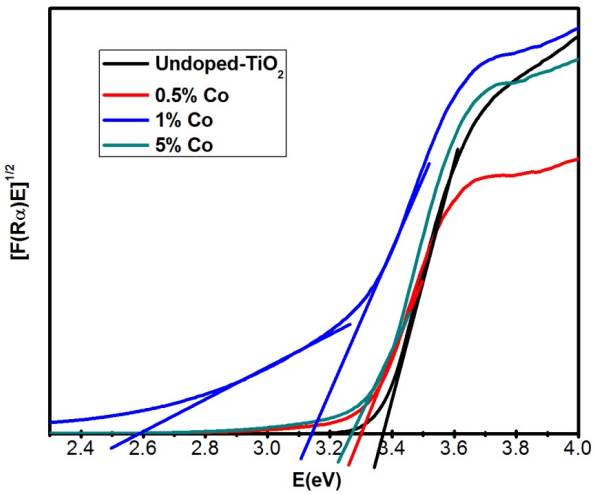

Figure 3. DRS calculated direct band gap of Co-doped TiO_2 catalyst with various Co doping contents at 0-5 mol%

visible light until color of RhB disappeared. The photodegradation of RhB was examined by the decrease of its absorbance at maximum wavelength (λ_{max}) via Helios UV-Vis spectrometer.

Results and Discussion

The XRD patterns of Degussa P25 and co-precipitated Co-doped TiO_2 with various concentrations calcined at 500°C for 3 h are illustrated in Figure 1. The diffraction peaks occurring at 25.3°, 37.8°, 48.0°, 54.1°, 55.08°, 62.6°, 68.8°, 70.3° and 75.2° are assigned to lattice planes (101), (004), (200), (211), (204), (116), (220) and (215), respectively. All lattice planes indicate to the patterns of pure tetragonal anatase phase of TiO_2. There was no trace of secondary phase corresponding to metallic cobalt or cobalt compound. The color of undoped-TiO_2 can be observed in white powder while all Co-doped TiO_2 samples appear in pale green and the color is deepened when the concentration of cobalt increases. It can suggest that cobalt cations are properly incorporated into TiO_2 and uniformly distributed in lattice. The average crystallite size of all catalysts was calculated using Debye-Scherrer's Equation

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where, D is crystallite size, k is the constant usually taken as 0.94, λ is the wavelength of X-ray radiation (0.154 nm), β is the full width at half maximum (FWHM) and θ is the diffraction angle. The calculated crystallite size of the calcined catalyst is shown in Table 1. At low doping content of Co, the crystalline size of the catalyst is smaller than the value of the undoped samples. It is suggest that the reduction of crystalline size occurred because of different ionic charges of Ti^{4+} and Co ions. Co dopant may substitute at Ti site leading to the crystalline defect, oxygen vacancy in TiO_2 structure and crystallization deterioration. By increasing Co dopant, the increasing in crystalline is observed (Samet *et al.* 2013 and Alamgir *et al.* 2014). The morphologies of co-precipitated Co-doped TiO_2 catalyst were observed by SEM image as displayed in Figure 2. These photographs illustrate highly dispersed spherical particles. By increasing Co dopant, the noticeable agglomeration is noticeable that is well agreeable to the calculated crystallite size of the catalyst results.

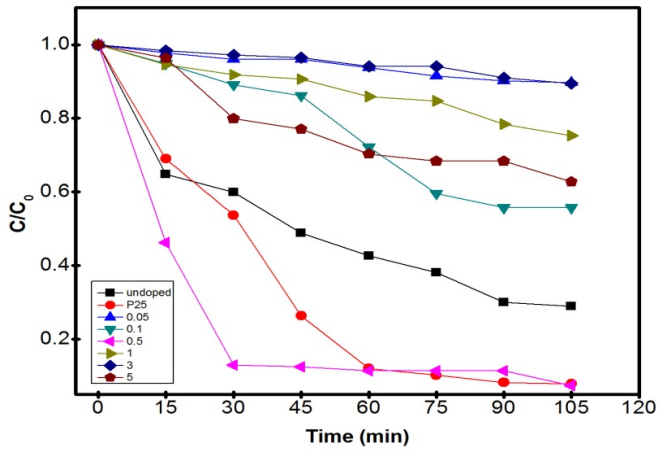

Figure 4. Photocatalytic degradation of RhB dye under visible irradiation of Degussa P25 and Co-doped TiO2 catalyst with various Co doping contents at 0-5 mol%

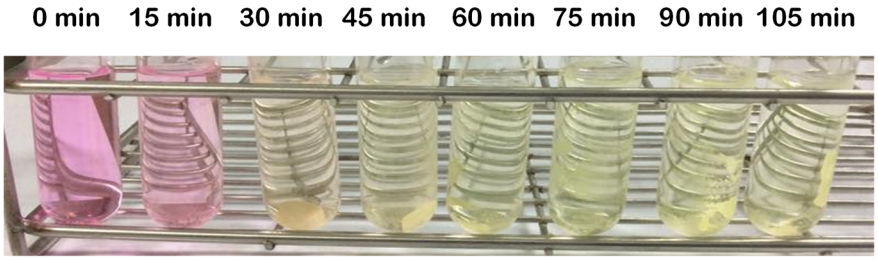

Figure 5.Photographs of color change of RhB dye under visible irradiation with 0.5% Co doped TiO_2 catalyst for 0-105 min

Table 1. calculated crystallite size of Degussa P25 and Co-doped TiO_2 catalyst with various Co doping contents at 0-5 mol% from Scherrer's equation

Samples	P25	Undoped TiO_2	0.1%	0.5%	1%	5%
Size (nm)	29.5	22.9	20.7	18.8	20.7	34.5

The DRS spectra of the catalyst exhibit the absorption spectrum increased in visible range. The DRS data were converted to Kubelka-Munk function F(R) by the Equation

$$F(R) = \frac{(1-R)^2}{2R} \qquad (2)$$

where, F(R) is absorption coefficient. The direct optical band gap (E_g) value is estimated relying on Tauc's relation.

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \quad (3)$$

where, α is the absorption coefficient, $h\nu$ is a photon energy, A is a constant and n =1/2 for direct or n = 2 for indirect allowed transition semiconductors. (Escobedo *et al.* 2006) The optical band gap indicates correlated photon energy during the photo reaction. By increasing Co dopant, the prominent absorption showed a red shift (500-800 nm) of the absorption in visible region. The existence of absorption peak in visible region is attributed to charge transfer interaction between Co and Ti ions (Gillapelli *et al.,* 2013). This may be a reason for high photoactivity in longer wavelength. The calculated direct band gaps of undoped-TiO_2, 0.5%, 1% and 5% Co-doped TiO_2 catalyst are found to be 3.37 eV, 3.29 eV, 3.26 eV and 3.14, 2.58 eV, respectively. It can be seen that the optical band gap significantly decreases with increasing Co doping content in TiO_2 as shown in Figure 3.

Photocatalytic activities of all catalysts were evaluated by degradation of RhB under visible light irradiation. Figure 4 presents the photocatalytic reaction of Co-doped TiO_2 with various Co dopants (0-5 mol%) comparing to Degussa P25. It clearly seen that 0.5 mol% of Co-doped TiO_2 catalyst demonstrates superiority in degradation efficiency. The complete de-colorization of RhB dye was achieved after 105 min of reaction under visible irradiation over partial degradation in the presence of commercial Degussa P25 and undoped-TiO_2. The photographs of decolorization of RhB dye under visible irradiation with 0.5% Co doped TiO_2 catalyst are taken from digital picture shown in Figure 5. The effective dye degradation affirms that Co dopant in catalyst can enhance the optical absorption in visible region and reduce its band gap. However, the increased crystallite size and decreased surface area of catalyst with increasing Co concentration dopant could be considered as major drawbacks. Moreover, overdoped Co ions in host matrix may act as reco mbination centers and consequently decrease the photocatalytic activity. (Peng *et al.,* 2015).

Conclusions

In summary, Co-doped TiO_2 catalysts were successfully synthesized by co-precipitation process. The XRD results show the presence of tetragonal anatase phase of TiO_2 with no trace of secondary phase corresponding to metallic cobalt or cobalt compound. It suggests that cobalt ions may be substituted lead to the crystalline defect and oxygen vacancy in TiO_2. The doping was found to cause agglomeration and the increase in crystallite size of the catalyst. Furthermore, the Co dopant plays significant role on the improvement in optical properties in visible region at 500-800 nm comparing to undoped TiO_2. It is noticed that the optical band gap gradually decreases (3.37-2.58 eV) with increasing Co dopant in TiO_2. The photocatalytic activity of RhB implies that 0.5% Co doped TiO_2 catalyst could effectively enhance the photodegradation under visible light irradiation compared with commercial Degussa P25.

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