One-pot Synthesis of Carbon-doped TiO$_2$ with Bimetallic Ni-Ag Co-catalysts in Photodegradation of Methylene Blue under UV and Visible Irradiation

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Abstract

Carbon modified-titanium dioxide (@C-TiO$_2$) was prepared by one-pot procedure from TiCl$_4$ and glucose under hydrothermal conditions at 150 °C for 24 hours. The obtained @C-TiO$_2$ was employed as support for Ni-Ag(3.0)@C-TiO$_2$ nanocomposite (3.0 is the Ni/Ag molar ratio). The synthesized catalysts were characterized by means of XRD and UV-Vis DRS Spectroscopy. The XRD patterns of @TiO$_2$ show the brookite as the main phase, meanwhile the main phase in the @C-TiO$_2$, Ni-Ag(3.0)@TiO$_2$ and Ni-Ag(3.0)@C-TiO$_2$ nanocomposites were anatase. The band gap of the TiO$_2$ sample slightly shifted to the visible range after the addition of C dopant or Ni-Ag(3.0) co-catalyst as indicated by UV-Vis DRS spectra. Ni-Ag(3.0)@C-TiO$_2$ catalyst showed high photocatalytic activity for photodegradation of MB under both UV and visible irradiations at 60 °C within 2 hours with maximum MB conversion of 67.5% and 54.1%, respectively. The synergistic action of C dopant or Ni-Ag(3.0) co-catalyst is believed to be important in the improvement of photocatalytic activity of @TiO$_2$. Copyright ©2019 BCREC Group. All rights reserved

Keywords: C-doped TiO$_2$; bimetallic Ni-Ag co-catalyst; methylene blue; photodegradation


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1. Introduction

Titanium dioxide (TiO$_2$)-based photocatalysis as a green chemistry technology has drawn considerable attention due to its extensively potential applications in the fields of organic pollutant degradation, environmental remediation, and solar energy conversion [1-5]. However, the application of pure TiO$_2$ is limited, because of it requires ultraviolet (UV) light, which makes up only a small fraction (<4%) of the total solar spectrum reaching the surface of the earth. Therefore, over the past few years, considerable efforts have been directed towards the improvement of the photocatalytic efficiency of TiO$_2$ in the visible-light region [6-8].

There are several notable efforts in the improvement of photocatalytic efficiency of TiO$_2$ in the visible-light region including the addition of second atoms as dopant both metal and non-metal dopants [8,9]. Various transition metals...
dopant have been evaluated, such as: vanadium (V), molybdenum (Mo), rhodium (Rh), and iron (Fe) and among them, iron was widely applied due to Fe$^{3+}$ has ionic radius of 0.79 Å which is very close to ionic radius of Ti$^{4+}$ resulting in easier for doping processes of ion Fe$^{3+}$ into TiO$_2$ [8-10] and demonstrated relatively high activity on the methylene blue photodecomposition within a 65 min of reaction time [11]. On the other hand, non metal dopants, such as: nitrogen (N), sulphur (S), and carbon (C) are also frequently employed to improve the sensitivity of TiO$_2$ towards visible-light resources [12-13]. For example, carbon doped-TiO$_2$ (C-TiO$_2$) with amount of carbon-doped around 5.2 %mol has lowest band-gap energy of 2.3-2.8 eV [12]. Several previous reports have also showed that C-TiO$_2$ catalysts were effective for the photodecomposition of acid orange 7 (AO7) with 99% conversion [14]. Teng et al. also reported the conversion of Rhodamine B using C-TiO$_2$ catalyst (with band-gap energy of 2.91 eV) and 95% conversion Rhodamine B was achieved under visible-light irradiation [15].

Beside the addition of dopant, the presence of co-catalysts could also enhance the photocatalytic efficiency of TiO$_2$ under visible light region. Various transition metals have been investigated and a significant improvement was also achieved [17-18]. Zhang et al. reported the use of vanadium (V), platinum (Pt), nickel (Ni), and chromium (Cr) as co-catalyst for photodegradation of methyl orange with 60% conversion which is higher than that of pure TiO$_2$ (30% conversion) [19]. Sung-suh et al. reported that the efficiency of Ag-TiO$_2$ increased almost three times during the photodegradation of Rhodamine under visible-light irradiation [20].

In the present work, we report the simple procedure for the synthesis of carbon-doped titanium oxide (@C(5.2%)-TiO$_2$; 5.2% is amount of C to TiO$_2$ in %wt) in one pot synthetic protocol from glucose and titanium tetrachloride (TiCl$_4$) as precursors of carbon and TiO$_2$, respectively, via hydrothermal treatment at 150 ºC for 24 h. Bimetallic nickel-silver (Ni-Ag(3.0); 3.0 is Ni/Ag molar ratio) catalysts, @both bulk and supported on @TiO$_2$ and @C-TiO$_2$ were also synthesized using a similar procedure to the previous reports [21-22]. The synthesized catalysts then were evaluated for the photodegradation of methylene blue in batch reactor system under both ultraviolet (UV) and visible (Vis) light irradiation at 60 ºC. The effect of reaction conditions and catalyst characterizations are discussed throughout the manuscript text.

2. Materials and Methods

2.1 Materials

Nickel chloride hexahydrate (NiCl$_2$.6H$_2$O 99.9%), silver nitrate (AgNO$_3$.99.8%), NaOH pellet 99.0%, D(+)-Glucose anhydrate, TiCl$_4$ 99.0%, HCl 37%, ethanol 96%, and ethylene glycol (EG) 99.5% were purchased from Merck Millipore and used as received. Sodium borohydrate (NaBH$_4$.95.0%) and methylene blue 70.0% were purchased from Tokyo Chemical Industry Ltd Co. (TCI).

2.2 Catalyst Preparation

2.2.1 Synthesis of @C-TiO$_2$

A typical procedure for the synthesis of carbon-doped titanium oxide (@C-TiO$_2$) is described as follows. A 2.0 M of TiCl$_4$ solution was prepared by diluting 100 mL TiCl$_4$ (99%, Merck) with 1.0 mL HCl 37% in 350 mL of deionized water [23]. Carbon-doped TiO$_2$ (@C(5.2%)-TiO$_2$; 5.2% %wt of C to TiO$_2$) was synthesized by mixing a glucose solution (~15 g/L) with 20 mL TiCl$_4$ (0.04 mol) solution at room temperature. The pH of mixture was adjusted by addition of NaOH 10 M dropwise un-
til pH = 10. The mixture was homogenized at 50 °C for 18 h then transferred into an autoclave-Teflon reactor for hydrothermal processes at 150 °C for 24 h. After finished, the reactor was cooled to room temperature and the precipitate was filtered, washed with absolute ethanol and followed by deionized water until pH become neutral and then dried at 80 °C for 3 h to obtain @C-TiO₂ powder.

2.2.2 Synthesis of Ni-Ag(3.0)@C-TiO₂

Synthesis of bimetallic nickel-silver supported on @C-TiO₂ (denoted as Ni-Ag(3.0)@C-TiO₂; 3.0 is Ni/Ag molar ratio) is described as follows [21-22]. A 0.8568 gram NiCl₂ 6H₂O (3.6 mmol) was dissolved in deionized water (5 mL) (denoted as solution A) and 0.2038 gram AgNO₃ (1.2 mmol) was dissolved in deionized water (5 mL) (denoted as solution B). Solution A and B, ethylene glycol (20 mL), NaOH (6 M, 3 mL) were mixed at room temperature while gently stirring while an one gram NaBH₄ was also added slowly. The mixture was transferred into an autoclave-Teflon reactor for hydrothermal processes at 150 °C for 24 h. After finished, the reactor was cooled to room temperature and the precipitate was filtered, washed with absolute ethanol and followed by deionized water until pH become neutral and then dried at 110 °C for 3 h to obtain Ni-Ag(3.0)@C-TiO₂ powder.

2.3 Catalyst Characterization

Powder X-ray diffraction (XRD) measurements were recorded on a Mac Science M18XHF instrument using monochromatic CuKα radiation (λ = 0.15418 nm). The XRD equipment operated at 40 kV and 200 mA with a step width of 0.02° and a scan speed of 4° min⁻¹ (α₁ = 0.1540 nm, α₂ = 0.1544 nm).

Analysis ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) was performed on an UV-Vis Shimadzu 2450 with double beam system at Affiliation Laboratory of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), University of Indonesia Jakarta BaSO₄ powder was used as standard material. The calculation of band-gap energy (Eg) was derived from the obtained spectra using a formula of $E_g = \frac{hC}{\lambda}$, whereas h is Planck constant (4.136×10⁻¹⁵ eV.s), C is light velocity (2.997×10⁸ m.s⁻¹), λc is cut-off wave length (nm). λc was derived from plotted data of absorbance versus wavelength with linear cross-section on the spectra (Tauc plot) [26-27].

The NH₃-TPD was carried out on a Belsorp Max (BEL Japan). The samples were degassed at elevated temperature of 100-200 °C for 2 h to remove physisorbed gases prior to the measurement. The temperature was then kept at 200 °C for 2 h while flushed with He gas. NH₃ gas (balanced NH₃, 80% and He, 20%) was introduced at 100 °C for 30 min, then evacuated by helium gas to remove the physisorbed also for 30 min. Finally, temperature programmed desorption was carried out at temperature of 100-900 °C and the desorbed NH₃ was monitored by TCD.

2.4 Photodegradation of Methylene Blue

A typical procedure for the photodegradation of methylene blue (MB) over Ni-Ag(3.0)@C-TiO₂ catalyst is described as follows. A solution of MB (100 ppm, 30 mL) and 0.15 g Ni-Ag(3.0)@C-TiO₂ were mixed in glass-tube reactor (50 mL) then immersed in water batch at 60 °C under UV or visible irradiations (UV or visible lamp sources are 4 x 8 W). The reaction mixture was stirred at 310 rpm for 30 min to reach the equilibrium point of adsorption-desorption. The reaction mixture was irradiated for 120 min at a reaction temperature of 60 °C and sampled every 30 min and analyzed by using Perkin Elmer UV-Vis double beam spectroscopy.

3. Results and Discussion

3.1 Catalyst Characterizations

Figure 3 shows the XRD patterns of the synthesized titanium oxide (@TiO₂), carbon (@C) and @C-TiO₂ nanocomposite. It can be observed that the brookite phase was predominantly formed in TiO₂ sample. A serial diffraction peak at 2θ = 25.78°, 26.86°, 31.24°, 40.32°,
44.94°, 53.4°, and 55.98° which can be recognized as TiO₂ brookite (120), (111), (121), (022), (032), and (241), respectively. Anatase phase was also observed at θ = 25.04°, 36.94° dan 53.4° which also can be assigned as TiO₂ anatase (101), (103), and (105), respectively. A single diffraction peak at θ = 28.10° that characteristic peaks of TiO₂ rutile (110) (Figure 3a). In the case of C-TiO₂ nanocomposite, the main phase of formed TiO₂ in @C-TiO₂ was anatase which can be easily recognized at θ = 24.48°, 36.94°, and 53.48° as TiO₂ anatase (101), (103), and (105), respectively. Ren et al. also reported that the use of glucose as precursor of carbon promoted the formation of TiO₂ anatase and inhibited TiO₂ brookite formation [24].

Figure 4 shows the XRD pattern of bulk Ni-Ag(3.0), Ni-Ag(3.0)@TiO₂, and Ni-Ag(3.0)@C-TiO₂. The formation of TiO₂ anatase (101) was observed at θ = 25.29° (Figure 3a) which is hardly to calculated the crystallite sizes due to the small peak. A sharp diffraction peak was observed at θ = 37.82° which can be recognized as Ag(111) in all samples (Figure 4). A series of TiO₂ anatase (101), (103), and (105) respectively. Ni(111)/Ag(200) at diffraction peaks at θ = 28.10°, 32.82°, and 45.99°, respectively were also clearly observed [25]. The crystallite sizes of Ni-Ag(110), Ag(111), and Ni(111)/Ag(200) in bulk Ni-Ag(3.0) sample were 23.40 nm, 22.73 nm, and 21.50 nm, respectively. In Ni-Ag(3.0)@TiO₂ sample, the crystallite sizes of bimetallic Ni-Ag alloy are unable to calculate using Scherrer equation.

Figure 5 shows the NH₃-TPD spectra of the synthesized @C-TiO₂, (b) Ni-Ag(3.0)@TiO₂, and (c) Ni-Ag(3.0)@C-TiO₂ and the total acidity also summarized in Table 1. The synthesized @TiO₂ has highest amount of acid sites (968 μmolg⁻¹) among the catalysts (entry 1) while the amount of acid sites of @C-TiO₂ nanocomposite slightly decreased to 822 μmolg⁻¹ (entry 2). Bulk Ni-Ag@TiO₂ consists of desorption peak at 183°C which can be attributed as a weak acidity. On the other hand, Ni-Ag(3.0)@C-TiO₂ comprises two desorption peaks at 210 °C and 498 °C which can be recognized as weak and medium acidities and the total amount of acid sites was 240 μmolg⁻¹ (entry 5).

Figure 6 displays the UV-Vis DRS spectra of each synthesized catalysts. The band-gap energy (E₉) was estimated from the plotting of absorbance (A) versus wavelength (nm) using Tauc plot and a formula of \( E_9 = \frac{h.c}{\lambda} \), where \( h \) is Planck constant, \( C \) is light velocity, and \( \lambda \) is cut-off wave length (nm) that derived from plotted data of absorbance versus wavelength [26-27]. It was found that the estimated band gap energies (E₉) of each synthesized catalysts

![Figure 3 XRD patterns of the synthesized (a) @C, (b) @TiO₂ and (c) @C-TiO₂ nanocomposite.](Image)

![Figure 4 XRD patterns of (a) Ni-Ag(3.0)@C-TiO₂, (b) Ni-Ag(3.0)@TiO₂ and (c) bulk Ni-Ag(3.0).](Image)
@TiO$_2$, @C-TiO$_2$, Ni-Ag(3.0)@TiO$_2$ and Ni-Ag(3.0)@C-TiO$_2$ were 2.96 eV, 2.57 eV, 2.84 eV, and 2.69 eV, respectively. These results indicate that the addition of dopant and co-catalyst significantly shifted the absorption band of @TiO$_2$ to the visible region as indicated by the $E_g$.

### 3.2 Photodegradation of Methylene Blue

Firstly, we carried out the photodegradation of methylene blue (MB) over various catalysts at temperature of 60 °C for 2 h and the results of UV-Vis absorption spectra of the remained MB are shown in Figure 7. By using @TiO$_2$ catalyst, a the photodegradation of MB was occurred slowly as indicated by a broadened peak of MB species after a reaction time of 2 h. It is found that the synthesized @C-TiO$_2$ catalyst was not active for MB photodegradation under the same reaction conditions. On the other hand, the amount of MB was significantly reduced in presence of Ni-Ag(3.0)@TiO$_2$ and Ni-Ag(3.0)@C-TiO$_2$ catalysts as indicated by the decreasing of intensity at $\lambda = 664$ nm which can be associated as the degradation of phenothiazin functional group and demethylation of N group in MB structure [16].

To obtain insight into the kinetic profiles of each the synthesized catalysts, the photodegradation of MB was monitored using UV-Vis spectrophotometer and the sampling was carried out at interval time of 30 min. The kinetic profiles of MB photodegradation over @TiO$_2$, @C-TiO$_2$, Ni-Ag(3.0)@TiO$_2$, and Ni-Ag(3.0)@C-TiO$_2$ catalysts are shown in Figures 8. General-
ly, except @C-TiO₂ catalyst (Figure 8b) exhibited lowest activity for MB photodegradation than the others catalysts. We also intentionally performed the photodegradation reaction of MB under visible irradiation instead of UV using the synthesized catalysts and the results are summarized in Table 2.

The amount of MB after pre-absorption onto the catalyst surface was determined after initial time of 30 min (denoted as $C_{t30}$), while the remained MB after a reaction time of 120 min (denoted as $C_{t120}$). The conversion of MB was calculated based on the remained MB to $C_{t30}$ from UV-visible spectroscopic method using standard curve technique. It is found that under UV irradiation, the amount of absorbed MB on the surface of @TiO₂, @C-TiO₂, and Ni-Ag@C-TiO₂ catalysts showed almost similar, which are 83.3 ppm, 83.8 ppm, and 88 ppm. Only Ni-Ag(3.0)@TiO₂ catalyst exhibited very high absorption capacity as indicated by the amount of remained MB after 30 min, c.a. 46.5 ppm and 27.4 ppm after irradiation with UV and visible, respectively.

In the case of @TiO₂ catalyst, conversion of MB under UV and visible irradiation was 51.0% and 56.4%, respectively (entries 1 and 2). Consistent with the results of kinetic profiles over @C-TiO₂ catalyst, the conversion of MB was only 10.9% and 13.5% (entries 3 and 4). On the other hand, a relatively high MB conversion was achieved over Ni-Ag(3.0)@TiO₂ after UV irradiation (53.4%, entry 5) while under visible irradiation was only 14.7% (entry 6). Interestingly, Ni-Ag(3.0)@C-TiO₂ demonstrated remarkable high conversion of MB both under UV and visible irradiations. These results suggest that the synergistic action between C dopant and bimetallic Ni-Ag co-catalyst during the MB photodegradation reaction [28-30].

4. Conclusion

We demonstrated the catalytic performance of @TiO₂, @C-TiO₂, Ni-Ag(3.0)@TiO₂, Ni-Ag(3.0)@C-TiO₂ catalysts on the photodegradation of MB under UV and visible irradiations at 60 °C after a reaction time of 120 min. Spectroscopic analysis using UV-Vis DRS confirmed that the addition of C dopant and bimetallic Ni-Ag co-catalyst significantly reduced the band gap energy ($E_g$) of @TiO₂. The band ener-

Figure 8. Reaction profiles of MB photodegradation over the synthesized (a) @TiO₂, b) @C-TiO₂, c) Ni-Ag(3.0)@TiO₂, and d) Ni-Ag(3.0)@C-TiO₂ catalysts under UV irradiation. Reaction conditions: catalyst (0.15 g), MB (100 ppm, 30 mL), reaction time (120 min), at 60 °C.

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能源 gap of each synthesized @TiO2, @C-TiO2, Ni-Ag(3.0)@TiO2, Ni-Ag(3.0)@C-TiO2 catalysts was 2.96 eV, 2.57 eV, 2.84 eV, and 2.69 eV, respectively. Ni-Ag(3.0)@C-TiO2 catalyst was found to be effective for photodegradation of MB under both UV and visible irradiations with maximum MB conversion of 67.5% and 54.1%, respectively after 120 min.

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