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TiO_2/Ag-nanoparticle as a Photocatalyst for Dyes Degradation

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Abstract Visible light active TiO_2/Ag-nanoparticle (TiO_2/Ag-NP) photocatalyst was prepared and tested for phenolic dye degradation. The dye photodegradation was performed in batch reaction under visible light irradiation for various predetermined times. The results showed that the increase in initial Ag(I) concentration caused the amount of Ag deposited on the TiO_2 solid to increase. However, no more Ag deposited into the TiO_2 phases was observed for further increase in Ag(I) concentration. Further, small amount of Ag(I) in the solution mixture gave Ag nanoparticles deposited on the TiO_2 phase, while high initial Ag(I) content produced large Ag aggregates. The dye photodegradation under visible light irradiation over TiO_2/Ag-NP was more effective than unmodified TiO_2. The increase in Ag content in the photocatalyst improved dye photodegradation reaction, while the further increase in Ag content led to decrease in the dye photodegradation. The dye photodegradation can be best performed for 45 min of visible light irradiation.

Keywords: TiO_2, Ag nanoparticle, photocatalyst, dye, photodegradation

1. Introduction

Titania (TiO_2) is well known semiconductor-based photocatalyst having apparent superiority over the rest materials due to its stability toward biological and chemical reactions, high redox ability, low cost, and benign to the environment (Fujishima *et al.*, 2000). As photocatalyst, it has wide band gaps, i.e. 3.2 eV for anatase phase and 3.0 eV for rutile phase. TiO_2 alone requires UV light for excitation to form photoactive species of holes (h^+) and electrons (e^-) (Fujishima *et al.*, 2000). The h^+ acts as strong oxidizing agent. Meanwhile the e^- works as reducing agent. The UV light is believed to be expensive to set up and poses health hazard. The recombination of h^+ and e^- in the TiO_2 photocatalyst is fast, causing ineffective photocatalytic process.

To overcome the photocatalytic limitation, TiO_2 has been subject to modification by doping with several noble metals including Au (Maicu *et al.*, 2011; Hidalgo *et al.*, 2011), Pt (Maicu *et al.*, 2011; Murcia *et al.*, 2014), Pd (Maicu *et al.*, 2011), and Ag (Sze and Barteau, 2006; Lenzi, *et al.*, 2010; Kochi *et al.*, 2010). The presence of the precious metals in the TiO_2 phase is believed to inhibit charge recombination since metallic particles serve as electron traps (Maichu *et al.*, 2011). Doping TiO_2 by noble metals results in better photocatalytic performance. Also, the modification of TiO_2 by precious metals gives photocatalyst that is active under visible light illumination, which provide wider and cheaper applications that the native TiO_2.

Among other precious metals, Ag is the cheapest one but has comparable photocatalytic performance. Several methods have been reported to prepare TiO_2/Ag-NP i.e. by chemical reduction (Sileikaite *et al.*, 2006; Guzman *et al.*, 2009; Qin *et al.*, 2010; Malina *et al.*, 2012; Kumar *et al.*, 2015), electrochemical reduction (Ma *et al.*, 2004), bioreduction (Mubarak *et al.*, 2011, Silambarasan and Jayanthi, 2013), sol-gel (Lenzi *et al.*, 2010; Koci *et al.*, 2010), and photoreduction (Sze and Barteau, 2005). Among the reported methods, the photocatalytic reduction induced by UV light has attracted much attention since it is very efficient and straightforward to design (Wahyuni *et al.*, 2015a; 2015b). So far, the preparation of TiO_2 doped with Ag by photoreduction has not been intensively explored.

In this contribution, we report on the preparation TiO_2/Ag-NP photocatalyst through photocatalytic reduction of Ag(I) over TiO_2. The photocatalytic activity of the product was tested for photodegradation reaction of phenolic dyes, which were frequently used in the textile industries.

2. Experimental Method

2.1 Chemicals and Equipments

Analytical grade of $AgNO_3$, TiO_2, and phenolic dye were purchased from Merck and were used without further purification. A Perkin-Elmer 3110 Series AAS, GBC-UV/Visible spectrophotometer, 6000X Shimadzu XRD, and Shimadzu-IR machines were used for product characterization and analysis. A set of photocatalytic reaction apparatus for batch Ag(I) photoreduction and dye photodegradation was used.

2.2. Procedure

The photocatalyst was prepared by photoreduction. The photoreduction of Ag(I) solution in the 250 mL solution was realized by irradiation with UV light in the presence of 1.0 g TiO_2 for 24 h as reported earlier (Wahyuni, 2009). The Ag(I) concentration was predetermined at 500, 1000, 1500, 2500, and 3500 mg/L. They were assigned as TiO_2/Ag-500, TiO_2/Ag-1000, TiO_2/Ag-1500, TiO_2/Ag-3500. After UV irradiation, the resulting solid was separated, and unreduced Ag(I) content was measured by AAS. The $Ag^{(0)}$ incorporated into the TiO_2 phases was calculated from the initial and final Ag(I) concentrations. The TiO_2/Ag-NP samples were dried at 120 °C for 2 h before characterization by XRD, FTIR, and TEM. The photodegradation of phenolic dye was done in the presence of the prepared material. Typically, TiO_2/Ag-NP with prescribed weight was added to a 100 mL solution containing 25 mg/L dye. The mixture was irradiated with visible light for certain period. The dye content in the solution before and after irradiation was evaluated by UV-Vis spectrophotometry.

3. Results And Discussion

3.1 Preparation and Characterization of TiO_2/Ag-NP

a. AAS analysis

The effect of the Ag(I) concentration on the Ag photoreduction and deposition on TiO_2 is presented in Fig. 1. It shows that high initial Ag(I) content gives more $Ag^{(0)}$ product. The photoreduction of Ag(I) ions to $Ag^{(0)}$ catalyzed by TiO_2 is presented in reactions (1) and (2). Upon excitation by UV-light, the TiO_2 solid produces holes (h^+) and electrons (e^-). The e^- was captured by Ag^+ ions to yield $Ag^{(0)}$.

$$TiO_2 + \text{UV light} \rightarrow TiO_2 + h^+ + e^- \tag{1}$$

$$Ag^+ + e^- \rightarrow Ag^0 \tag{2}$$

The increase in the initial Ag(I) concentrations does not give additional Ag photoreduction product. It is believed that the e^- produced by the photocatalytic reaction is limited. The high concentration of Ag(I) will reduce the UV light intensity. Also, the surface of TiO_2 may be blocked by Ag particles that have been produced previously from the photoreduction. It will prevent further reaction between Ag(I) in the solution with TiO_2 photocatalyst.

b. XRD analysis

The XRD patterns of the prepared TiO_2/Ag-NP were presented in Fig. 2. It shows similar diffraction patterns for all TiO_2/Ag-NP produced and TiO_2. It indicates that after photoreduction process, the TiO_2 phases remained unchanged. The peaks of $Ag^{(0)}$ that correspond to the *fcc* crystal system was not observed since the Ag content in the TiO_2 solids is small.

The reduced Ag may be deposited on the TiO_2 surface. It results in the TiO_2 XRD peak intensity to reduce. The $Ag^{(0)}$ is also believed to be dispersed in the TiO_2 solid as indicated by TEM images.

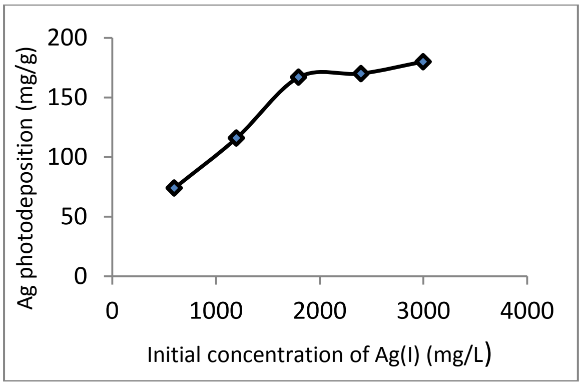


Fig. 1 The effect of the initial Ag(I) concentration on the Ag photoreduction

c. IR analysis

The IR spectra of prepared TiO_2/Ag-NP are displayed in Fig. 3. The FTIR spectra of TiO_2/Ag-NP is similar to that of TiO_2. A slight shift in IR peak at 540 and 679 cm^{-1} for TiO_2 to 556 and 694 cm^{-1} for TiO_2/Ag-NP was observed. The peak at 540 and 679 cm^{-1} is attributed to the TiO_2 vibration mode of -O-Ti-O- in the presence of Ag in TiO_2/Ag-NP (Kochi *et al.*, 2010).

d. TEM imaging

Fig. 4 shows the TEM images of TiO_2 and prepared TiO_2/Ag-NP. It indicates that there are small dark dots on the surface of TiO_2 particles. The dots can be attributed to $Ag^{(0)}$ particles, the product of photoreduction of Ag(I). It is similar to the results reported earlier (Sze and Barteau, 2005; Bo *et al.*, 2015).

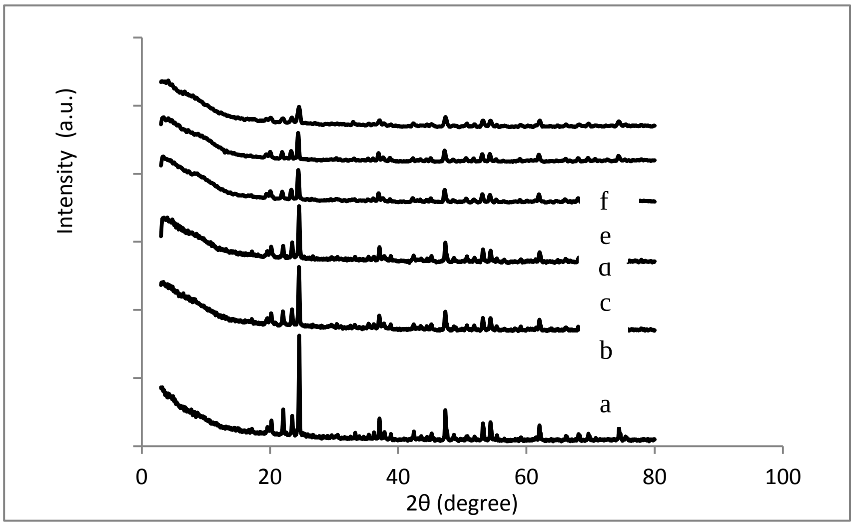


Fig.2. XRD patterns of (a) TiO_2, (b) TiO_2/Ag-500, (c) TiO_2/Ag-1000, (d) TiO_2/Ag-1500, (e) TiO_2/Ag-2500, and (f) TiO_2/Ag-3500

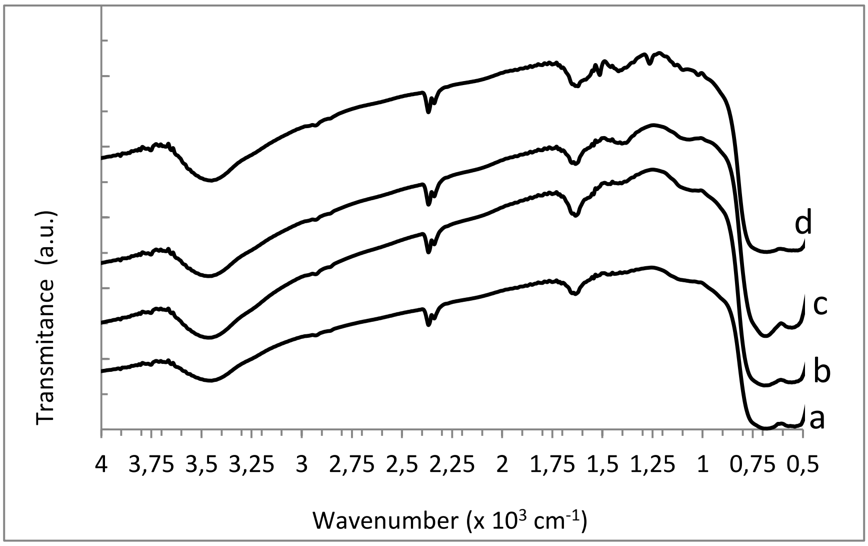
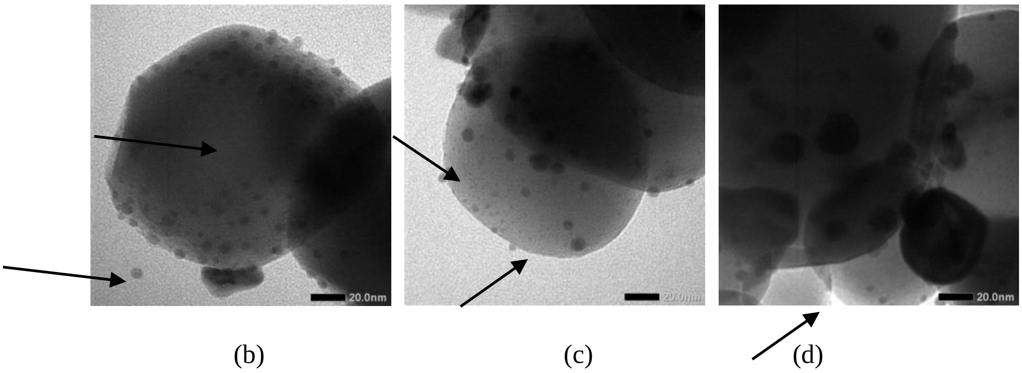


Fig.3. IR spectra of (a) TiO_2, (b) TiO_2/Ag-500, (c) TiO_2/Ag-1500, (d) TiO_2/Ag-3500



(b) (c) (d)

Fig.4. The TEM images of (a) TiO_2/Ag-500, (b) TiO_2/Ag-1500, (c) TiO_2/Ag-3500

The Ag nanoparticles are well-dispersed in the TiO_2 solid as indicated in the TEM images. The number of the darker dots are larger when Ag(I) concentration is high. The Ag(I) content at 500 and 1500 mg/L produces Ag nanoparticles with the diameter <20 nm. On the other hand, the high initial Ag(I) concentration (3500 mg/L) gives Ag nanoparticle with diameter >20 nm.

The small amount of Ag(I) allows the Ag crystal growth to be well-confined by the TiO_2 structure. On the other hand, larger Ag(I) concentration will produce Ag nanoparticles with bigger particle size, which is controlled well by the TiO_2 structure.

3.2. Photocatalytic Activity

The activity of TiO_2/Ag-NP was tested for phenolic dye photodegradation under visible light. The results were presented in Fig. 6. The photocatalytic reactions were written as the reactions (8) and (9).

$TiO_2 + \text{light} \rightarrow TiO_2 + e^- + h^+$ (3)
$h^+ + \text{dye} \rightarrow \text{dye}^*$ (4)
$\text{dye}^* \rightarrow CO_2 + H_2O$ (5)
$h^+ + H_2O \rightarrow H^+ + HO\cdot$ (6)
$HO\cdot + \text{dye} \rightarrow CO_2 + H_2O$ (7)
$h^+ + e^- + TiO_2 \rightarrow TiO_2$ (8)

Reaction (3) represents the formation of photoactive species so-called hole (h^+) that behaves as powerful oxidizing agent (Fujishima, *et al*. 2000). When the dye molecule captures h^+, it becomes unstable, as indicated by reaction (4). The dye degrades and forms small molecules of CO_2 and H_2O, as presented in (7). At the same time, the recombination of e^- and h^+ occurs concurrently, as represented in reaction (8).

As shown in Figure 6, the degree of the dye photodegradation catalyzed by TiO_2/Ag-NP was larger than the one catalyzed by unmodified TiO_2. The photodegradation takes place after the dye captures e^- produced by TiO_2 during the visible light irradiation [Fujishima, 2008]. The electron capture by Ag metal will maintain h^+ and $HO\cdot$ concentration high, which can promote dye photodegradation. The recombination h^+ and $HO\cdot$ causes dye photodegradation to slow down. Note that the visible light cannot excite TiO_2 to yield e^-, h^+ and $HO\cdot$.

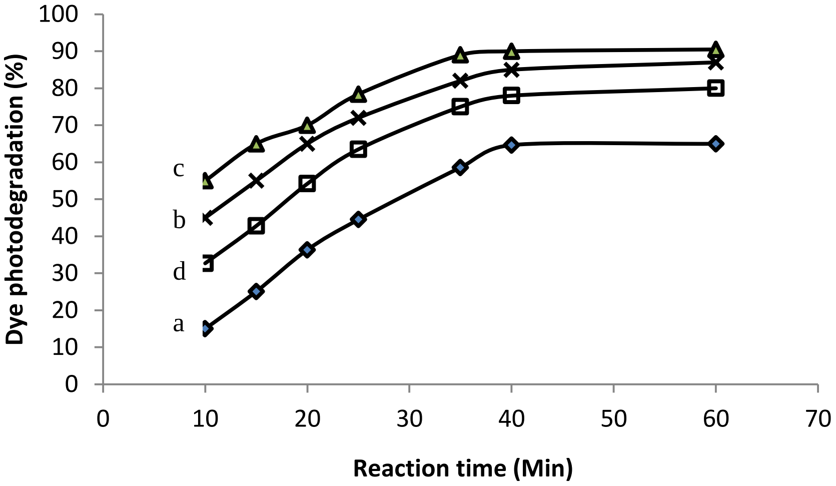


Fig.6. The influence of irradiation time and Ag amount in TiO_2/Ag-NP on the dye Photodegradation, over (a) TiO_2, (b) TiO_2/Ag-500, (c) TiO_2/Ag-1500, (d) TiO_2/Ag-3500

The Ag content in the TiO_2/Ag-NP solid affects the dye photodegradation. Photocatalyst with high Ag content degrades more dye molecules. Ag nanoparticles are believed to capture electron released by TiO_2 during visible light illumination. When the e^- species are taken by Ag nanoparticles, more h^+ and OH• radicals are available in the reaction system. Thus, it can improve dye photodegradation. However, significant amount of Ag in the TiO_2/Ag-NP surface causes the dye photodegradation to decrease. Ag nanoparticles could block visible light to excite TiO_2, which produce small amount of h^+ and HO• radicals that are responsible for the dye photodegradation.

It is expected that the dye photodegradation is time-dependent. Long irradiation time leads to more dye molecules to be degraded. The h^+ and HO• are continuously produced when the TiO_2/Ag-NP photocatalyst is illuminated with visible light. However, long reaction time does not show more dye molecules to be degraded. The photocatalyst solid seems to be used up after visible light illumination is prolonged.

4. Conclusion

The Ag nanoparticle was successfully incorporated into the TiO_2 polycrystalline solid by photoreduction reaction to yield TiO_2/Ag-NP. The Ag particle size was dependent on the Ag(I) concentration in the solution where small starting Ag(I) level produced nano-sized particles with smaller size. The TiO_2/Ag-NP showed better photocatalytic phenolic dye degradation under visible light illumination than of the unmodified TiO_2. The TiO_2 containing small nano-sized Ag particles also shows better photocatalytic degradation than TiO_2 containing larger nano-sized Ag particles. Also, the dye photodegradation was affected by Ag loading and reaction time. The TiO_2/Ag-1500 has the best photocatalytic performance with illumination time of 24 h.

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