Chapter 8

Photoreduction Processes over TiO_2 Photocatalyst

Endang Tri Wahyuni and Nurul Hidayat Aprilita

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.80914

Abstract

This chapter presents the study of TiO_2 photocatalyst for the photoreduction of several reducible chemicals. The photocatalytic reduction of several toxic metal ions, including Ag (I), Cu(II), Cr(VI), Hg(II), and U(VI) in the presence of TiO_2, in order to decrease their toxicity, is described. Photodeposition of the noble metals, such as Ag(I), Au(III), Pt(IV), and Pd(II) for doping purposes by photocatalytic reduction over TiO_2, is also addressed. Conversion of the greenhouse gas of CO_2 into useful hydrocarbons and methanol by photocatalytic reduction using TiO_2 photocatalyst is highlighted. Several operating parameters in photoreduction processes that are photocatalyst dose, time of the irradiation, pH of the solution, and the initial concentration of the substrates (the reducible chemicals) are also reviewed.

Keywords: photoreduction, TiO_2 photocatalyst, detoxification, doping, CO_2 conversion

1. Introduction

Semiconductor TiO_2 is regarded as one of the most promising photocatalysts, because it has low cost and high activity, good physical and chemical stability, and nontoxic property [1]. The structure of a semiconductor is characterized by two bands, called as valence band and conduction band, that are separated by a gap named as bandgap energy (Eg). The first band is filled by electrons, while the second is empty or no electron occupying it. The bandgap of TiO_2 with anatase typed is 3.2 and 3.0 eV is for the rutile type [2]. Both anatase and rutile are tetragonal in structure, but the anatase has octahedrons that share four edges forming the fourfold axis.

The photocatalyst of TiO_2 works by absorption of UV to near visible region, with the energy same as or higher than its bandgap (light with a wavelength of 365 nm is required by rutile and that of 411 nm is for anatase) that generates electron and hole pair. The pair generation is resulted by excitation of some electrons from valence band (e_{vb}) to the conduction one (e_{cb}) with the formation of positive holes ($h_{vb}+$) [3, 4]. The reactions of electron–hole generation from TiO_2 are presented as Eqs. (1):

$$TiO_2 + h\nu \rightarrow TiO_2\left(e^- + h^+\right) \quad (1)$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (2)$$

$$h^+ + TiOH \rightarrow Ti\ OH \quad (3)$$

$$e^- + O_2 \rightarrow {O_2}^- \quad (4)$$

$$TiO_2 + \left(e^- + h^+\right) \rightarrow TiO_2 + heat \quad (5)$$

Notes: *hv* represents photon energy of UV light *(E = hv)*, $O_2{}^-$ is called as superoxide, and ·OH indicates hydroxide radical.

The electrons, in water media and in the presence of dissolve oxygen, can react with the oxygen to form super oxide, as presented by reaction (4) [4]. This is a reduction path. The use of the electrons from TiO_2 for some reducible metal ions such as Ag(I) [5–13], Au(III) [13–17], Cr(VI) [18–23], Cu (II) [24–26], Hg(II) [27, 28], and U(VI) [29, 30] has also been developed.

Meanwhile the hole generates the free OH radical after contact with water and TiO_2 surface, as illustrated by Eq. (2) and (3). The OH radical acts as a strong oxidizing agent with high oxidation potential (E^0 = 2.8 V) that can degrade organic compounds into smaller CO_2 and H_2O molecules [3, 4]. This is called as oxidation path. Due to strong ability in organic degradation, OH radicals from TiO_2 have been intensively applied for cyanide oxidation [31], treating hazardous phenol [32, 33], di-nitrophenol [34, 35], various organic dyes [36–39], and surfactant of detergent [40].

The applications of the photodegradation process catalyzed by TiO_2 have been frequently published through journals and books. Meanwhile, less intensive photoreduction methods are explored. In fact, the photoreduction process over TiO_2 has some advantages compared to the other reduction reactions, with respect to simplicity, cost-effectiveness, efficiency, less chemical usage, and green chemistry principles.

It is interesting therefore to address the applications of the reduction over TiO_2 photocatalyst for various purposes. The applications of the photocatalytic reduction in the presence of TiO_2 for detoxifying the toxic metal ions, doping by transition and noble metals, and converting greenhouse gas CO_2 into more valuable chemicals are described in more detail.

2. Photocatalytic reduction over TiO_2 to detoxify metal ions

The reducible hazardous heavy metal ions that are widely found in the wastewater are silver Ag(I), copper Cu(II), hexavalent chromium Cr(VI), mercury Hg(II), and uranium U(VI). Silver pollutant can be found with high concentration in the wastewater of radiophotography activity that is usually disposed from hospitals [41, 42], silver electroplating, and electronic fabrication [43].

Wastewaters containing copper in high concentration are disposed from electroplating and electrical stuffs [43, 44]. Hexavalent chromium is mostly emitted by metal plating activity and paint industry [45, 46]. Mercury is usually contained in wastewater originated from gold recovery and incinerator in hospitals [46, 47]. The environmental contamination by uranium (VI) ion may originate from uranium purification or extraction from its respected mineral. A leak of nuclear reactor releasing uranium into the water may also contribute to the uranium contamination [48, 49].

Contamination of the hazardous metals can create environmental and human health problems. Silver contamination can induce argyria syndrome [50]. For human, the excessive copper intake can disturb the gastrointestinal (GI) system [44]. Hexavalent chromium is carcinogenic [45, 51], and mercury Hg(II) can cause neurological dysfunction [47]. The uranium ion, as a radioactive element, must be very dangerous, both for environment and human [44]. Therefore, a method that can detoxify the hazardous heavy metals is urgently.

The products of the reduction of Ag(I), copper Cu(II), hexavalent chromium Cr(VI), mercury Hg(II), and uranium (VI) are Ag(0), Cu(0), Cr(III), Hg(0), and U(IV), respectively, that are less toxic [44]. Hence, these facts motivate many researchers for detoxification of the hazardous heavy metal ions by reduction method, especially by photoreduction catalyzed by TiO_2.

Photoreduction of Ag(I) ions in the aqueous solution by electron provided by TiO_2 takes place effectively, due to its high standard reduction potential (E^0) = 0.79 V [52]. The reaction is presented by Eq. (6) that produces undissolved solid silver that is less toxic and easier to be handled. It is clear that by photoreduction process, the silver contaminant is detoxified:

$$Ag^+ + e^- \rightarrow Ag^0 \qquad E^0 = 0.79\ V \tag{6}$$

Hexavalent chromium in the aqueous solution existed as chromate ($CrO_4^=$) and bichromat ($Cr_2O_7^=$) ions, depending on the pH that has high standard reduction potential (E^0) = 1.33 V in acid condition [52]. This allows them to be easily reduced into Cr(III) as Cr^{3+} ions as presented by reaction (7). The chromate (Cr(VI)) is highly toxic, while Cr^{3+} is less toxic or is even needed by feeding women [45]. Hence, detoxification of the toxic Cr(VI) can be carried out by reduction method. Photoreduction of Cr(VI) over TiO_2 photocatalyst has been frequently reported [18–23] with satisfaction result. Further, the Cr^{3+} ions can precipitate into undissolved $Cr(OH)_3$ in basic condition that is remediable by solidification/stabilization technique:

$$Cr_2O_7^= + 14H^+ + e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad E^0 = 1.52\ V \tag{7}$$

Copper ions in the solution formed as Cu^{2+} can be reduced into dissolved Cu (I) and/or undissolved Cu(0), with respective E^0 = 0.153 V and 0.34 V [52]. Photoreduction method in the presence of TiO_2 has been subjected to detoxify the toxic Cu^{2+} that can prominently form the undissolved toxic Cu(0), with very small Cu(I) ion [24–26]. The reactions of the Cu(II) reduction are shown by Eqs. (8) and (9). The photoreduction of Cu(II) is found to be less effective compared to Ag(I) photoreduction that may be caused by the low standard reduction potential, E^0 = 0.34 V [52]. To improve the effectiveness, a reducing agent, such as oxalic acid, can be added in the Cu(II) photoreduction [26]:

$$Cu^{2+} + e \rightarrow Cu^{+} \qquad E^0 = 0.153\ V \tag{8}$$

$$Cu^{2+} + 2\ e \rightarrow Cu^{0} \qquad E^0 = 0.34\ V \tag{9}$$

Photoreduction over TiO_2 has been also used to detoxify mercury (Hg^{2+}) ion in the aqueous solution, by converting it to be undissolved Hg^0 [27, 28]. Based on the standard reduction potential as seen in the reaction (10) [52], the reduction should proceed effectively. To handle the elemental or solid mercury may be easier than that of the dissolved ions. As presented by previous authors [47], the order of the toxicity level of mercury forms, from the most toxic, is methyl mercury (CH_3Hg), $Hg^{(0)}$ vapor, Hg^{2+} dissolved ion, and $Hg^{(0)}$ element:

$$Hg^{2+} + 2e^{-} \rightarrow Hg^{0} \qquad E^0 = 0.85\ V \tag{10}$$

The photoreduction catalyzed by TiO_2 suspension has also been studied for removal of the radioactive uranium (VI) [48, 49] that exists as $UO_2{}^{2+}$ anionic in the solution. The anion is the most stable form and so the one that is found in the solution. The photoreduction of the anionic has produced the less radioactive uranium (V), Eq. (11) [52]:

$$UO_2{}^{2+} + e^{-} \rightarrow UO_2{}^{+} \qquad E^0 = 0.163\ V \tag{11}$$

Detoxification of the hazardous (toxic and radioactive) heavy metals by photoreduction pathway offers a simple, practical, economic, and green procedure that meets with the future requirement method in solving the environmental pollution problem.

3. Photoreduction method over TiO_2 for metal recovery and doping purposes

Photoreduction of some reducible metal ions results in the solid phase deposited on the TiO_2 structure. This deposition phenomenon has inspired some researchers to use the photoreduction for metal recovery and doping purposes.

Recovery is objected to get pure valuable metals such as silver (Ag) and gold (Au) from the regarding solution, by applying the photoreduction method. The photoreduction of Ag(I) follows Eq. (6). To take the pure Ag particles from Ag deposited on TiO_2, one can use ultrasonic shaker [12].

Photodeposition for gold recovery can also be obtained through reduction under UV light in the presence of TiO_2 photocatalyst [17]. In this step, the gold is dissolved in the aqueous solution formed as Au^{3+} ions and then to be reduced as shown by reaction (12):

$$Au^{3+} + 3e^{-} \rightarrow Au^{0} \qquad E^0 = 1.32\ V \tag{12}$$

Doping, whether with transition and noble metals on TiO_2 recently, has attracted much attention, since it can improve the performance of TiO_2 as a photocatalyst under UV light, as well as shift the absorption of TiO_2 to visible light region [5–11]. The latter is supposed to give some advantages, as the photocatalytic process under metal-doped TiO_2 can take place under sun light that must be low-cost and safer and so greener than that of by UV light irradiation.

The transition metals that have been examined as dopants on TiO_2 are Cu(II) [53, 54], Fe [55, 56], Co [56, 57], Ni [57], Mn [56], and Cr [58]. Moreover, Ag(I) [5–13], Au(III) [13, 14], Pd(II) [14], and Pt(IV) [14] are the noble metals that are frequently doped into TiO_2 structure. All the metals doped on TiO_2 are reported to improve the photocatalytic activity of TiO_2 under UV irradiation as well as to shift the visible absorption with various effects, from very low, shown by Cr(III) up to the very significant effect, observed on Ag(I).

A doping process basically involves the conversion of the metal ions in the solution to be deposited solid metal on TiO_2 powder that is frequently carried out by sol–gel method [56]. However, hydrothermal [57] and chemical vapor [58] methods are also introduced.

From the above methods, the regard salt solution is usually used as the dopant source, and high temperature is required that makes the method costly due to high energy consumption. In addition, large metal particle is usually resulted from the process that retards the metal insertion into gap of valence and conduction gaps. As a consequence, the small absorption shift is resulted that yields less significant improvement of the photocatalyst activity under UV light or the slight visible light responsiveness.

In addition to the four doping methods, photoreduction has also been examined. The photoreduction method becomes a great of interest, because the process takes place at room temperature, no need of chemicals, except UV light, and has resulted small cluster of metal dopant particles. The small particles are well inserted into the gap between valence and conduction band of TiO_2. Such insertion has considerably shortened the gap that enhances the activity under UV light and pronounces shift of the light absorption into wide visible region. However, the photoreduction method is limited only for dopants that are reducible metal ions, including Cu(II) representing transition metal and Ag(I), Au(III), Pd(II), and Pt(IV) for noble metal ions.

In general, the doping process by photoreduction method is carried out by UV light irradiation toward the regard metal salt solutions in a certain period of time. Then M/TiO_2 (M = metal dopant) resulted is dried at about 110°C to remove the water.

Photoreduction of Ag (I) in the solution over TiO_2 for doping purpose principally follows the same procedure as in the detoxification, as described earlier. The starting salt for Ag doping usually used is $AgNO_3$ [5–13].

As its high standard reduction potential (E^0), the photoreduction of Ag^+ takes place efficiently, and the small Ag particle resulted can enter into the gap between the conduction and the valence. The present of the small particle dopant in the gap shortens the bandgap. This allows the metal-doped TiO_2 to be active under visible light and to work better with UV irradiation, whether for degradation of the organic pollutants or for bacterial combating.

In the doping Au on TiO_2 through photoreduction method, the salt frequently introduced as gold source is $KAuCl_4$ that dissolves to form $AuCl_4^-$ [13–16]. The doping follows reaction (13). The other gold ions may form as $AuCl_2^-$, Au^+, and Au^{3+} that are also reducible by the following reactions (14)–(16) with their own standard reduction potentials [52]:

$$AuCl_4^{-} + 3e^{-} \rightarrow Au^0 + 2Cl_2 \qquad E^0 = 0.93\ V \tag{13}$$

$$Au^{+} + e^{-} \rightarrow Au^0 \qquad E^0 = 1.83\ V \tag{14}$$

$$Au^{3+} + 3e^{-} \rightarrow Au^0 \qquad E^0 = 1.32\ V \tag{15}$$

$$AuCl_2^{-} + e^{-} \rightarrow Au^0 + Cl_2 \qquad E^0 = 1.15\ V \tag{16}$$

The gold atom resulted from the photoreduction is doped on TiO_2 structure or TiO_2/Au through insertion or impregnation. The doped photocatalyst has been tested for phenol degradation under UV light and showed more satisfaction result than undoped TiO_2 [13].

Platinum (Pt) doped TiO_2 or TiO_2/Pt can be resulted by irradiating H_2PtCl_6 salt in the aqueous solution in the presence of TiO_2 suspension [14]. The platinum salt is dissolved to form an ion of $PtCl_4^{4+}$ and/or Pt^{2+} ions, and the reactions of the photoreduction are represented by Eqs. (17) and (18) [52]:

$$PtCl_4^{2-} + 2e^{-} \rightarrow Pt^0 + 2Cl_2 \qquad E^0 = 0.77\ V \tag{17}$$

$$Pt^2 + +2e \rightarrow Pt^0 \qquad E^0 = 1.20\ V \tag{18}$$

Photoreduction of Pd(II) over TiO_2 for the doping purpose is performed by the irradiation of $PdCl_2$ in the aqueous solution with UV light [14]. The reduction of Pd(II) ion is written as reaction (19) that yields small Pd particles on TiO_2 structure:

$$Pd^2 + +2e^{-} \rightarrow Pd^0 \qquad E^0 = 0.915\ V \tag{19}$$

With the same conditions of the photoreduction, it is found that the order of the photodeposition efficiency from the highest is shown by Pt (100%) that is followed by Au (80%) and then by Pd (50%). This sequence photoreduction result is consistent with their standard reduction potentials that are 1.2, 0.93, and 0.915 V, as well as their empirical radii that are 135, 135, and 140, respectively. The higher standard reduction potentials promote more reduction, and smaller size facilitates the effective insertion. They have also been examined for phenol degradation and displayed the effective results [14].

4. Photoreduction method over TiO_2 of the greenhouse gas CO_2 into valuable substances

The level of CO_2 that is a primary greenhouse gas in the atmosphere is continuously rising that creates serious global warming. Conversion of CO_2 into more valuable compounds is believed to be the best way in preventing the excess CO_2 disposal in the air. CO_2 is a thermodynamically stable and chemically inert compound, and it is difficult to oxidize or to reduce it to other useful compounds under normal operating conditions.

http://dx.doi.org/10.5772/intechopen.80914

Therefore, converting CO_2 into valuable products is possible when catalytic, electrocatalytic, plasmatic, enzymatic, and photocatalytic reduction processes [59] are employed. Among them, photocatalytic reduction seems to be the most intensively developed method.

The photoreduction of CO_2 with water vapor catalyzed by titania-based photocatalysts results in methane (CH_4), methanol (CH_3OH), carbon monoxide (CO), formic acid (HCOOH), and formaldehyde (HCHO) and follows the simplified reactions (20)–(23) [59].

$$2CO_2 + 4H_2O \rightarrow 2CH_3OH + 3O_2 \tag{20}$$

$$3CO_2 + 2H_2O \rightarrow CH_4 + 2CO + 3O_2 \tag{21}$$

$$CO_2 + 2H_2O \rightarrow 2HCOOH + O_2 \tag{22}$$

$$CO_2 + 2H_2O \rightarrow HCOH + O_2 \tag{23}$$

The conversion reaction pathways are not specific and mainly depend on the reaction conditions. This is therefore a complex mechanism that proceeds through branching pathways and produces different products simultaneously [59].

Reduction of CO_2 in the presence of NaOH solution photocatalyzed by TiO_2 supported on a polymer has been reported to produce methanol and methane, accompanied with formic acid and formaldehyde. The CO_2 is being soluble in NaOH solution and forms carbonate and bicarbonate ions based on the pH measurement. The reductions of carbonate acid and carbonate ions with their standard reduction potential are shown as Eqs. (24) and (25) [60]:

$$H_2CO_3 + 6H^+ + 6e^- \rightarrow CH_3OH + 2H_2O \qquad E^0 = 0.044\ V \tag{24}$$

$$CO_3^{2-} + 8H^+ + 6e^- \rightarrow CH_3OH + 2H_2O \qquad E^0 = 0.209\ V \tag{25}$$

From the equations, based on the standard reduction potential reduction, the photoreduction of carbonate ions (mostly existing in higher pH) to form methanol takes place faster or is more effective than the photoreduction of the carbonate acid.

Various mechanistic reaction schemes have been proposed for CO_2 reduction with H_2O using TiO_2 photocatalysts. The following are the reaction mechanisms proposed for methane formation [61]:

$$H_2O + 2h^+ \rightarrow \cdot OH + H\cdot \tag{26}$$

$$CO_2 + e^- \rightarrow CO_2\cdot \tag{27}$$

$$2CO_2\cdot + 2e \rightarrow 2CO\cdot + O_2 \tag{28}$$

$$2CO\cdot + 4H\cdot \rightarrow 2\cdot CH_2 + O_2 \tag{29}$$

$$2\cdot CH_2 + 2H\cdot \rightarrow 2CH_4 \tag{30}$$

The above mechanism steps start with the reaction between water molecule with the hole or positive radical from TiO_2 (Eq. (1)) to form radicals of OH and H (Eq. (26)). At the same time, carbon dioxide is reduced by the electron from Eq. (1), to form negative radical of carbon dioxide (Eq. (27)). The further reduction of CO_2 radical is preceded into carbon monoxide radical and oxygen (Eq. (28)). The CO radical then reacts with hydrogen radical from Eq. (26) to produce radical of methylene (Eq. (29)). Finally the methylene radical reacts with hydrogen radical to yield methane (Eq. (30)).

Different mechanisms for hydrogen, carbon monoxide, methane, and methanol productions are also proposed as seen in Eqs. (31)–(33) [62]. In this mechanism, only electron plays a role in the photoreduction, while no involvement of the hole is illustrated. Firstly, carbon dioxide gas reacts with the electron released from TiO_2 (Eq. (1)), to form anion of carbon dioxide (Eq. (31)). At same time, the hydrogen ion from water is also reduced by the electron to form hydrogen gas (Eq. (32)). Secondly, the anion of carbon dioxide reacts with hydrogen ion in the presence of electron to result carbon monoxide and water (Eq. (33)). In addition, the reaction of carbon dioxide anion with hydrogen ion and electron also occurred to produce methane and oxygen (Eq. (34)). Simultaneously, the carbon dioxide anion also reacts with the hydrogen ion and electron to yield methanol and water (Eq. (35)):

$$CO_2 + e^- \rightarrow CO_2^- \tag{31}$$

$$2H^+ + e^- \rightarrow H_2 \tag{32}$$

$$CO_2^- + 2H^+ + e^- \rightarrow CO + H_2O \tag{33}$$

$$CO_2^- + 2H^+ + e^- \rightarrow CH_4 + O_2 \tag{34}$$

$$CO_2^- + 2H^+ + e^- \rightarrow CH_3OH + H_2O \tag{35}$$

The methane and hydrogen gas resulted from photoreduction of CO_2 with H_2O under UV light and over TiO_2 is also formulated by mechanisms as follows [63]. The reactions between water molecule with a hole or positive radical photogenerated by TiO_2 under UV light irradiation (Eq. (36)) yield OH radicals and H ion (Eq. (37)). Then the OH radical further reacts with water and the positive radical, to release oxygen gas and hydrogen ion (Eq. (38)). The overall of the reactions (37) and (38) is represented by Eq. (39):

$$TiO_2 + \mathit{UV\ light} \rightarrow TiO_2 + e^- + h^+ \tag{36}$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \tag{37}$$

$$\cdot OH + H_2O + 3h^+ \rightarrow O_2 + 3H^+ \tag{38}$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \tag{39}$$

On the other side, CO_2 meets with the electron to form a corresponding radical (Eq. (40)). Then the radical is dissociated into carbon monoxide radical along with oxygen (Eq. (41)). The carbon monoxide radical is further split into carbon radical and oxygen (Eq. (42)). The overall reaction is written as Eq. (43):

$$CO_2 + e \rightarrow \cdot CO_2 \tag{40}$$

$$\cdot CO_2 \rightarrow \cdot CO + 1/2O_2 \tag{41}$$

$$\cdot CO \rightarrow \cdot C + 1/2O_2 \tag{42}$$

$$CO_2 \rightarrow \cdot C + O_2 \tag{43}$$

The hydrogen ion obtained from the reaction (39) then reacts with the carbon radical from reaction (43) to yield methane and hydrogen gas, as represented by Eqs. (44) and (45), respectively:

$$4H^+ + \cdot C + 4e \rightarrow CH_4 \tag{44}$$

$$2H^+ + 2e \rightarrow H_2 \tag{45}$$

The following is the other mechanism in forming methanol, methane, and ethylene that is proposed [64–66]. After being released from TiO_2 (Eq. (46)), the hole reacts with water molecule to form radicals of hydroxyl and hydrogen (Eq. (47)), while the electron reduces the carbon dioxide to yield its anionic form (Eq. (48)). Then the anion of carbon dioxide reacts with the hydrogen radical from Eq. (47), to result an intermediate radical and hydroxide anion (Eq. (49)):

$$TiO_2 + UV\ light \rightarrow TiO_2 + e^- + h^+ \tag{46}$$

$$2H_2O + 2h^+ \rightarrow \cdot OH + H\cdot \tag{47}$$

$$CO_2 + e^- \rightarrow {CO_2}^- \tag{48}$$

$${CO_2}^- + 2H\cdot \rightarrow OC\cdot H + OH^- \tag{49}$$

$$OC\cdot H + OC\cdot H \rightarrow HOCCOH \tag{50}$$

$$HOCCOH + 4H\cdot \rightarrow CH_3COH \tag{51}$$

$$CH_3COH + H\cdot \rightarrow \cdot CH_3 + CO \tag{52}$$

$$\cdot CH_3 + H\cdot \rightarrow CH_4 \tag{53}$$

$$\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6 \tag{54}$$

The product of the radical (Eq. (50)) reacts with hydrogen radical to produce acetic acid (Eq. (51)). The acid can also further react with hydrogen radical to form methyl radical (Eq. (52)). Next, the methyl radical reacts with hydrogen to produce methane. When two methyl radicals react to each other, ethane is produced (Eq. (54)).

5. Variables influencing the photoreduction process

In the study of the photocatalytic reduction method, it is found that some variables including photocatalyst dose, reaction time, UV lamp types, pH, and concentration of the reducible ions considerably play an important role in the photoreduction results.

5.1. The influence of the photocatalyst dose

In general, the increase of the photocatalyst dose promotes higher photoreduction efficiency, and then it declines when the photocatalyst dose is further increased. Such trend can be explained in terms of the number of active sites available for photocatalytic reactions. The larger number of the active sites is available in as the dose of the photocatalyst increases that would generate more numbers of electrons and so higher photoreduction effectiveness. However, the large amount of catalyst may result in agglomeration form with larger particle size [40] that may provide smaller surface area. The agglomeration can also induce light scattering that reduces the light contacting with TiO_2 surface.

The smaller surface area can reduce the number of active sites and so decreases the electron number provided. Consequently lower photoreduction is obtained. Another reason of the decrease in the photoreduction can be attributed to the increase in the turbidity of suspension due to the large amount of photocatalyst. This leads to the inhibition of photon absorption by the photocatalyst. As an effect, the lesser photoinduced electrons can be provided, causing the photoreduction decreased [23]. From several studies, the optimum photocatalyst dose was reported to be 2 g/L (Ag(I)) [8], 1.6 g/L (Cr(VI)) [20], 0.1 g/L (Cu(II)) [25], and 2 g/L (Hg(I)) [27].

5.2. The influence of the reaction time

The reaction time determines how long is the contact between light with photocatalyst and that of electrons with the reducible metal ions. The general trend observed is that the photoreduction efficiency improves as the ratio of time is further extended. Longer than the optimum time, the photoreduction is usually independent on the reaction time. In the beginning and further extension time, the contact between light and TiO_2 becomes more effective, resulting in more number of electrons. Then, the extension time allows more effective contact between the electrons available with the reducible metal ions. This can enhance significantly the photoreduction. At one time, the photoreduction reaches maximum level, showing the optimum reaction time. For longer time than the optimum one, a very large amount of the products has been resulted that may prevent the contact among the reacting agents. Consequently, TiO_2 is hindered to release more electrons that give no increase in the photoreduction. The other reason is the reducible ions in the solution have been completely reduced that no more ions are left in the solution. The optimum reaction time is detected to be varied: 50–60 min and 5 h for Ag(I) [5, 10], 4 h for Cr(VI) [23], 3 h for Cu(II) [25], and 50–150 min for Hg (II) [27].

http://dx.doi.org/10.5772/intechopen.80914

5.3. The influence of pH

The other important variable is pH, since pH determines the species of both TiO_2 surface and the reducible metal ions that further affect in the photoreduction efficiency [12]. The general trend of the metal ion photoreduction efficiency with the alteration pH is that at the low pH, the photoreduction is usually low, and then increasing pH in the acid range gives a rise in the photoreduction results, but the further increasing pH leads to the photoreduction decreased. In the aqueous media, the low pH provides more amount of hydrogen ion H^+ that can interact with TiOH (TiO_2 hydrated) surface to form Ti $\cdot OH_2^+$. Such protonated titanol Ti $\cdot OH_2^+$ is more difficult to release electrons [2–4], although the metal ions mostly existed as the species that are easier to be reduced in large amount; the low photoreduction efficiency is usually observed. It is clear that the number of the electrons plays a prominent role on the photoreduction process.

Increasing pH in the acid range, the H^+ concentration declines that make TiOH available increased. This can raise the release of the electrons, and the metal ions are found as reducible species, so the photodegradation can be considerably enhanced. Finally, the number of OH may be in excess at higher pH that can create negative surface of TiO_2 to form TiO^-. This can retard the electron released. On the other side, generally the metal ions are precipitated with the hydroxide anions to form $M(OH)_n$ (M = metal, n = valence) that is impossible to be reduced. These two situations stimulate the negative effect on the photoreduction. As the other variables, there are also optimum pH values that are varied depending on the respective metal ions. Optimum pH value for Ag is found at 6–7 [8], at pH = 2 for Cr(VI) [23], and for Cu(II) is 2–3.5 [26], and pH = 4–4.1 is reported for Hg(II) [27]. The photoreduction of CO_2 with maximum results is observed at pH 4 [40].

5.4. The influence of the initial concentration

The initial concentration of the reducible metal ions is also important to be paid of attention in the photoreduction. In general, the relationship of the initial concentration is as follows: in the increase of the initial concentration, the metal ions in the photoreduction are enhanced. When the amount of the reduced ions is compared/relative to the initial concentration, it is usually observed that the photoreduction percentage decreases as the initial concentration increases. With the low initial concentration, the small number of the reducible ions is present with abundant electrons that can be reduced completely or 100%. By increasing the initial concentration of the metal ion, the number of the metal ions to be reduced is also increased, but the percentage is usually decreased. The optimum initial concentrations are reported to be 4×10^{-3} mole/L for Ag (I) [8], 3×10^{-3} mole/L for Cu(II) [24], 10 mg/L for Cr(VI) [23], 100 mg/L for Hg(II) [28], and the CO_2/H_2O ratio is 1/2 [66].

6. Conclusions

Photocatalytic reduction over TiO_2 has shown as an attractive method that can be applied for solving the environmental problems due to the toxic metal ion contamination, providing new and renewable energy by conversion of CO_2 into syngas, improvement TiO_2 photocatalyst activity under UV and solar light by doping process, and recovery of valuable economic metals based on the metal deposited.

Author details

Endang Tri Wahyuni* and Nurul Hidayat Aprilita

*Address all correspondence to: endang_triw@ugm.ac.id

Chemistry Department, Faculty of Mathematic and Natural Sciences, Gadjah Mada University, Indonesia

References

[1] Fujishima A, Rao TN, Tryk DA. Titanium dioxide photocatalysis. Journal of Photochemistry and Photobiology C. 2000;**1**:1-21

[2] Hoffmann MR, Martin ST, Choi W, And Bahnemann DW. Environmental Applications of Semiconductor Photocatalysis. Chemical Reviews. 1995;**95**:69-96

[3] Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO_2 surfaces: Principles, mechanisms, and selected results. Chemical Reviews. 1995;**95**:735-758

[4] Nakata K, Fujishima A. TiO_2 photocatalysis: Design and applications. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2012;**13**:169-189

[5] Seery MK, George R, Floris P, Pillai C. Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry. 2007;**189**:258-263

[6] Sung-Suh HM, Choi JR, Hah HJ, Koo SM, Bae YC. Comparison of Ag deposition effects on the photocatalytic activity of nanoparticulate TiO_2 under visible and UV light irradiation. Journal of Photochemistry and Photobiology A: Chemistry. 2004;**163**:37-44

[7] Guin D, Manorama SV, Latha JNL, Singh S. Photoreduction of silver on bare and colloidal TiO_2 nanoparticles/nanotubes: Synthesis, characterization, and tested for antibacterial outcome. Journal of Physical Chemistry C. 2017;**111**:13393-13397

[8] Anandan P, Kumar S, Pugazhenthiran N, Madhavan J, Maruthamuthu P. Effect of loaded silver nanoparticles on TiO_2 for photocatalytic degradation of Acid Red 88. Solar Energy Materials & Solar Cells. 2008;**92**:929-937

[9] Sobana N, Muruganadhan M, Swaminathan M. Nano-Ag particles doped TiO_2 for efficient photodegradation of Direct azo dyes. International Journal of Molecular Sciences. 2006;**13**:13275-13293

[10] Sobana N, Selvam K, Swaminathan M. Optimization of photocatalytic degradation conditions of Direct Red 23 using nano-Ag doped TiO_2. Separation and Purification Technology. 2008;**62**:648-653

[11] Kumar R, Rashid J, Barakat MA. Zero valent Ag deposited TiO_2 for the efficient photocatalysis of methylene blue under UV-C light irradiation. Colloids and Interface Science Communications. 2015;**2**:1-4

[12] Wahyuni ET, Aprilita NH, Mudasir M. Influence of Cu(II) on Ag(I) recovery by photocatalytic reduction method with TiO_2 suspension. Journal of Chemistry and Chemical Engineering. 2013;**4**(9):50-53

[13] Chan SC, Barteau MA. Preparation of highly uniform Ag/TiO_2 and Au/TiO_2 supported nanoparticle catalysts by photodeposition. Langmuir. 2005;**21**:5588-5595

[14] Maicu M, Hidalgo MC, Colón G, Navío JA. Comparative study of the photodeposition of Pt, Au and Pd on pre-sulphated TiO_2 for the photocatalytic decomposition of phenol. Journal of Photochemistry and Photobiology A: Chemistry. 2011;**217**:275-283

[15] Hidalgo MC, Murcia JJ, Navío JA, Colón G. Photodeposition of gold on titanium dioxide for photocatalytic phenol oxidation. Applied Catalysis A: General. 2011;**397**:112-120

[16] Zhang D. Photocatalytic applications of Au deposited on TiO_2 nanocomposite catalyst in dye degradation via photoreduction. Russian Journal of Physical Chemistry A. 2012;**86**(3): 498-503

[17] Wahyuni ET, Kuncaka A, Sutarno S. Application of photocatalytic reduction method with TiO_2 for gold recovery. American Journal of Applied Chemistry. 2015;**3**(6):207-211

[18] Iwata T, Ishikawa R, Ichino R, Okido M. Photocatalytic reduction of Cr(VI) on TiO film formed by anodizing. Surface and Coatings Technology. 2003;**169–170**:703-706

[19] Djellabi R, Ghorab RFM, Nouacer S, Smara A, Khireddine Q. Cr(VI) photocatalytic reduction under sunlight followed by Cr(III) extraction from TiO_2 surface. Materials Letters. 2016;**176**:106-109

[20] Chen G, Feng J, Wang W, Yin Y, Liu H. Photocatalytic removal of hexavalent chromium by newly designed and highly reductive TiO_2 nanocrystals. Water Research. 2017;**108**: 383-390

[21] Lei XF, Xue XX, Yang H. Preparation and characterization of Ag-doped TiO_2 nanomaterials and their photocatalytic reduction of Cr(VI) under visible light. Applied Surface Science. 2014;**321**:396-403

[22] Ma CM, Shen YS, Lin PH. Photoreduction of Cr(VI) ions in aqueous solutions by UV/TiO_2 photocatalytic processes. Journal of Photoenergy. 2012;**2012**. Article ID 381971:7

[23] Wahyuni1 ET, Aprilita1 NH, Hatimah H, Wulandari AM, Mudasir M. Removal of toxic metal ions in water by photocatalytic method. American Chemical Science Journal. 2015; **5**(2):194-201

[24] Barakat MA, Chen YT, Huang CP. Removal of toxic cyanide and Cu(II) Ions from water by illuminated TiO_2 catalyst. Applied Catalysis B: Environmental. 2004;**53**:13-20

[25] Satyro S, Marotta R, Clarizia L, Somma ID, Vitiello G, Dezotti M, et al. Removal of EDDS and copper from waters by TiO2 photocatalysis under simulated UV–solar conditions. Chemical Engineering Journal. 2014;**251**:257-268

[26] Kanki T, Yoneda H, Sano N, Toyoda A, Nagai C. Photocatalytic reduction and deposition of metallic ions in aqueous phase. Chemical Engineering Journal. 2004;**97**:77-81

[27] Lenzi GG, Fávero CVB, Colpin LMS, Bernabe H, Baesso ML, Specchia S, et al. Photocatalytic reduction of Hg(II) on TiO_2 and Ag/TiO_2 prepared by the sol–gel and impregnation methods. Desalination. 2011;**270**:241-247

[28] Khalil LB, Rophael MW, Mourad WE. The removal of the toxic Hg(II) salts from water by photocatalysis. Applied Catalysis B: Environmental. 2001;**36**:125-130

[29] Li Z-J, Huang Z-W, Guo W-L, Wang L, Zheng L-R, Chai Z-F, et al. Enhanced photocatalytic removal of Uranium(VI) from aqueous solution by magnetic TiO_2/Fe_3O_4 and its graphene composite in environmental science & technology. Environmental Science & Technology. 2017;**51**(10):5666-5674

[30] Jiang X-H, Xing Q-J, Luo X-B, Li F, Zou J-P, Liu S-S, et al. Simultaneous photoreduction of Uranium(VI) and photooxidation of Arsenic(III) in aqueous solution gC_3N_4/TiO_2 over hetero structured catalysts under simulated sunlight irradiation. Applied Catalysis B: Environmental. 2018;**228**:29-38

[31] Aguado J, van Grieken R, López-Muñoz MJ, Marugán J. Removal of cyanides in waste-water by supported TiO2-based photocatalysts. Catalysis Today. 2002;**75**:95-102

[32] Turki A, Guillard C, Dappozze F, Ksibi Z, Berhault G, Kochkar H. Phenol photocatalytic degradation over anisotropic TiO_2 nanomaterials: Kinetic study, adsorption isotherms and formal mechanisms. Applied Catalysis B: Environmental. 2015;**163**:404-410

[33] Choquette-Labbé M, Shewa WA, Jerald A, Lalman JA, Shanmugam SR. Photocatalytic degradation of phenol and phenol derivatives using a nano-TiO_2 catalyst: Integrating quantitative and qualitative factors using response surface methodology. Watermark. 2014;**6**:1785-1806

[34] Nakano K, Obuchi E, Takagi S, Yamamoto R, Tanizaki T, Taketomi M, et al. Photocatalytic treatment of water containing dinitropheno L, and city water over TiO_2/SiO_2. Separation and Purification Technology. 2004;**34**:67-72

[35] Shukla SS, Dorris KL, Chikkaveeraiah BV. Photocatalytic degradation of 2,4-dinitrophenol. Journal of Hazardous Materials. 2009;**164**:310-314

[36] Khataeea AR, Kasiri MB. Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: Influence of the chemical structure of dyes. Journal of Molecular Catalysis A: Chemical. 2010;**328**(1–2):8-26

[37] Vinu R, Akki SU, Madras G. Investigation of dye functional group on the photocatalytic degradation of dyes by nano-TiO_2. Journal of Hazardous Materials. 2010;**176**(1–3):765-773

[38] Dariani RS, Esmaeili A, Mortezaali A, Dehghanpou S. Photocatalytic reaction and degradation of methylene blue on TiO_2 nano-sized particles. Optik: International Journal for Light and Electron Optics. 2016;**127**:7143-7154

[39] Alahiane S, Sennaoui A, Sakr F, Qourzal S, Dinne M, Assabbane A. A study of the photocatalytic degradation of the textile dye Reactive Yellow 17 in aqueous solution by TiO2-coated non-woven fibres in a batch photoreactor. Journal of Materials and Environmental Sciences. 2017;**8**(10):3556-3563

[40] Wahyuni ET, Roto R, Sabrina M, Anggraini V, Leswana NF, Vionita AC. Photodegradation of detergent anionic surfactant in wastewater using UV/TiO_2/H_2O_2 and UV/Fe^{2+}/H_2O_2 processes. American Journal of Applied Chemistry. 2016;**4**(5):174-180

[41] Cappel CR, Cooley AC, Dagon TJ, Jenkins P, Robillard KA. Photographic Silver and the Environment. Rochester, New York: Eastman Kodak Company; 1992

[42] Dufficy TJ, Cappel CR, Summers SM. Silver discharge regulations questioned. Water Environment and Technology. 1993;**5**(4):52-56

[43] Concise International Chemical Assessment. Silver and Silver Compounds: Environmental Aspects. Geneva: WHO; 2002

[44] U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Chromium VI. Washington, DC: National Center for Environmental Assessment, Office of Research and Development; 1999

[45] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Chromium. Atlanta, GA: U.S. Public Health Service, U.S. Department of Health and Human Services; 1998

[46] Cushnie GC. Electroplating Wastewater Pollution Control Technology. New Jersey: Noyes Publication; 1985. p. 375377

[47] Emmanuel J, Orris P. Mercury: Its Properties, Sources and Health Effects. United Nations Development Program Global Environment Facility Global Project on Health Care Waste; 2005. pp. 10-12

[48] Akpor OB, Ohiobor GO, Olaolu TD. Heavy metal pollutants in wastewater effluents: Sources, effects and remediation. Advances in Bioscience and Bioengineering. 2014;**2**(4): 37-43

[49] European Commission DG ENV. E3. 2002. Heavy metals in waste final report. Project Environment, COWI A/S, Denmark, Europe, 1–86

[50] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Uranium (Update). Atlanta, GA: Public Health Service, U.S. Department of Health and Human Services; 1999

[51] Yoong LS, Chong FK, Dutt BK. Development of copper-doped TiO_2 photocatalyst for hydrogen production under visible light. Energy. 2009;**34**(10):1652-1661

[52] Gonell F, Puga AV, Lópeza B, García H, Corma A. Copper-doped titania photocatalysts for simultaneous reduction of CO_2 and production of H_2 from aqueous sulfide. Applied Catalysis B: Environmental. 2016;**180**:263-270

[53] Wang W, Zhang J, Chen F, He D, Anpo M. Preparation and photocatalytic properties of Fe^{3+}-doped Ag@TiO_2 core-shell nanoparticles. Journal of Colloid and Interface Science. 2008;**323**(43):182-186

[54] U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on Uranium, Natural. Washington, DC: National Centre for Environmental Assessment, Office of Research and Development; 1999

[55] Bard AJ, Parsons R, Jordan J. Standard Potentials in Aqueous Solutions. New York: Marcel Dekker; 1985

[56] Razali MH, Fauzi AMN, Mohamed AR, Sreekantan S. Morphological, structural and optical properties study of transition metal ions doped TiO_2 nanotubes prepared by hydrothermal method. International Journal of Materials, Mechanics and Manufacturing. 2013;**1**(4)

[57] Siddhapara K, Shah DV. Study of photocatalytic activity and properties of transition metal ions doped nanocrystalline TiO_2 prepared by Sol-Gel method. Advances in Materials Science and Engineering. 2014;**2014**. Article ID 462198:4

[58] Khakpash N, Simchi A, Jafari T. Adsorption and solar light activity of transition-metal doped TiO2 nanoparticles as semiconductor photocatalyst. Journal of Materials Science: Materials in Electronics. 2012;**23**:659-667

[59] Al-Ahmed A. Metal doped TiO_2 photocatalysts for CO_2 photoreduction. Materials Science Forum. 2013;**757**:243-256

[60] Lo C-C, Hung C-H, Yuan C-S, Hung Y-L. Parameter effects and reaction pathways of photoreduction of CO_2 over TiO_2/SO_4^{2-} photocatalyst. Chinese Journal of Catalysis. 2007; **28**(6):528-534

[61] Tan SS, Zou L, Hu E. Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO2 pellets. Catalysis Today. 2006;**115**:269-273

[62] Akhter P, Hussain M, Saracco G, Russo N. Novel nanostructured-TiO_2 materials for the photocatalytic reduction of CO_2 greenhouse gas to hydrocarbons and syngas. Fuel. 2015; **149**:55-65

[63] Shehzadad N, Tahir M, Joharia K, Murugesana T, Hussai M. A critical review on TiO_2 based photocatalytic CO_2 reduction system: Strategies to improve efficiency. Journal of CO_2 Utilization. 2018;**26**:98-122

[64] Oluwafunmilola OM, Maroto-Valer M. Transition metal oxide based TiO_2 nanoparticles for visible light induced CO_2 photoreduction. Applied Catalysis A: General. 2015;**502**:114-121

[65] Abdullah H, Khan MR, Pudukudy M, Yaakob Z, Ismail NA. CeO_2-TiO_2 as a visible light active catalyst for the photoreduction of CO_2 to methanol. Journal of Rare Earths. 2015; **33**(11):1155

[66] Liu S, Zhao Z, Wang Z. Photocatalytic reduction of carbon dioxide using sol–gel derived titania-supported CoPc catalysts. Photochemical & Photobiological Sciences. 2007;**6**:695-700