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# Photocatalytic Hydrogenation on Semiconductor Particles

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Additional information is available at the end of the chapter

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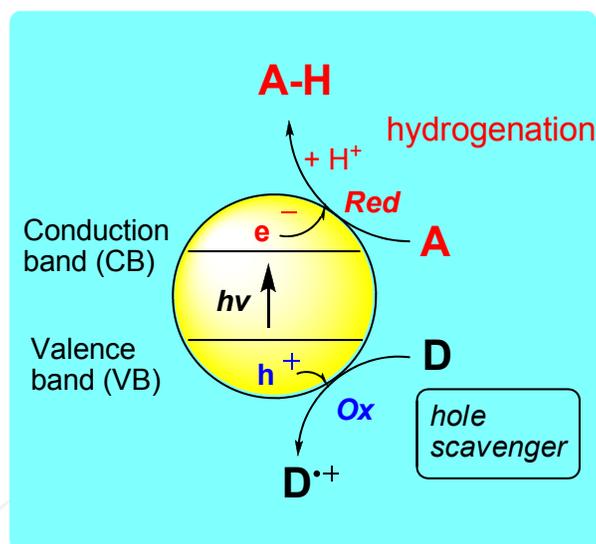
## 1. Introduction

Photocatalytic hydrogenation on semiconductor particles is a quite unique methodology compared to the conventional hydrogenations such as catalytic hydrogenation on metals or homogeneous catalysis using metal complexes. The catalysis can be defined as a light-driven redox reaction at a solid/liquid or a solid/gas interface. The semiconductor photocatalysis have been mainly developed by researchers in the areas of photochemistry, electrochemistry, and heterogeneous catalysis. Since Fujishima and Honda have discovered the photoelectrochemical water splitting upon titanium dioxide (TiO<sub>2</sub>) photoelectrode in the early 1970's [1], the heterogeneous photocatalysis, especially using TiO<sub>2</sub>, has been applied to various fields such as storage of solar energy [2,3], environmental purification [3,4], and specific surface properties of self-cleaning, self-sterilizing, and anti-fogging induced by incident light [5]. The photocatalysis has also attracted much attention with respect to inducing characteristic organic transformations since 1970's [6-11]. Among those, the photocatalytic hydrogenation of ethene and ethyne on TiO<sub>2</sub> was already reported in 1975 [12]. Since then, the reductive photocatalysis has been applied to the hydrogenation for several organic compounds having various double or triple bonds.

Herein, we summarize the progress in photocatalytic hydrogenations covering the literatures available up to 2011. At first, we introduce the fundamentals of semiconductor photocatalysis in order to understand the mechanistic principles. Next, we review the reports on applications to the photocatalytic hydrogenation. Here, we refer to scope and limitation of the photocatalytic hydrogenation on semiconductor particles. Advantages and disadvantages using this method are also compared to those of the conventional hydrogenations. Finally, prospects of the photocatalytic hydrogenation are discussed.

## 2. Fundamentals

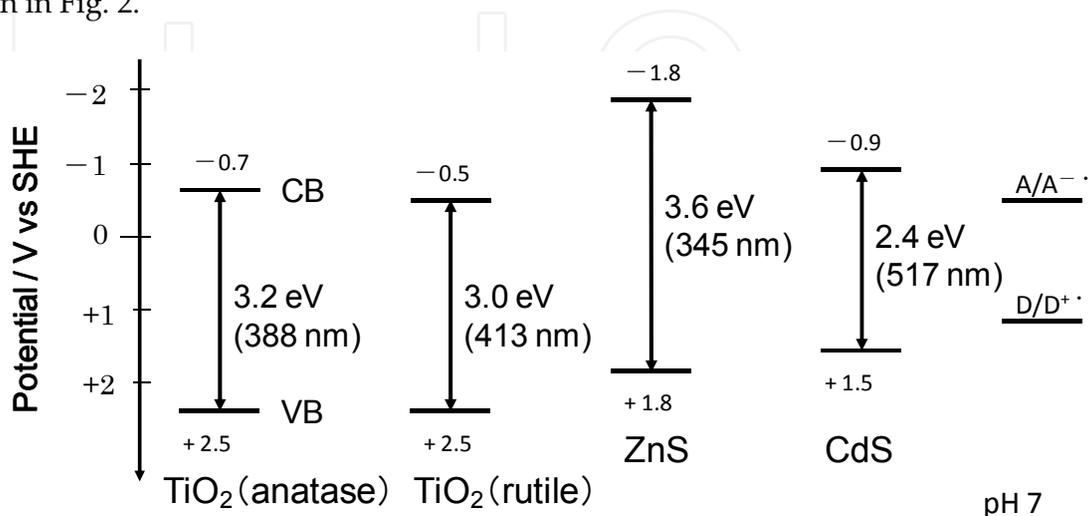
Some metal oxides (e.g. titanium dioxide ( $\text{TiO}_2$ ) etc.) and sulfides (e.g. cadmium sulfide ( $\text{CdS}$ ), zinc sulfide ( $\text{ZnS}$ ) etc.) are regarded as semiconductors, in which electrons ( $e^-$ ) photogenerated in conduction band (CB) and holes ( $h^+$ ) simultaneously generated in valence band (VB) play important roles in electroconductivity as well as chemical reactivities on the surface, i.e.  $e^-$  and  $h^+$  can induce redox reactions as shown in Fig. 1. This reaction system is so called “a micro-photoelectrochemical cell”, consisting of an anode and a cathode within a small particle. The hydrogenation generally proceeds as the reduction of an electron acceptor (**A**) followed by the protonation as depicted in Fig. 1. The photocatalytic reduction of **A** can be carried out in the presence of a large excess amount of electron donor (**D**) such as alcohols or amines, and in the absence of molecular oxygen ( $\text{O}_2$ ). The aim using the electron donor (**D**) is to scavenge hole generated in VB, thereby diminishing the degree of recombination between  $e^-$  and  $h^+$  within the semiconductor particles. Thus, it is important for the reductive hydrogenation of organic substrates to choose an appropriate electron donor (**D**) as hole scavenger. Moreover, it is necessary to purge  $\text{O}_2$  gas from the reaction system in order to improve the reduction efficiency, since  $\text{O}_2$  acts as a competitive electron acceptor.



**Figure 1.** Mechanistic principle of photocatalytic hydrogenation on a semiconductor particle

Important points in the semiconductor photocatalyst materials are band gap energy between CB and VB and potential energy levels of CB and VB. The band gap energy defines the minimum photon energy absorbed by the semiconductor materials: Band gap (eV) =  $1240/\text{wavelength (nm)}$ . Therefore, if a photocatalyst possesses less than 3.1 eV band gap, it can absorb photons with visible light region ( $> 400 \text{ nm}$ ). Fig. 2 indicates the band gaps and the band levels (V vs. standard hydrogen electrode (SHE) at pH 7) of  $\text{TiO}_2$  (anatase),  $\text{TiO}_2$  (rutile),  $\text{ZnS}$ , and  $\text{CdS}$  semiconductor materials as measured photoelectrochemically [8].  $\text{TiO}_2$  has four polymorphs: rutile (tetragonal, the most stable phase), anatase (tetragonal), brookite (orthorhombic), and  $\text{TiO}_2$  (B) (monoclinic), in which rutile and anatase have been

mainly used as photocatalysts. The band gap of anatase (3.2 eV) is slightly larger than that of rutile (3.0 eV), because the CB level of anatase is located at 0.2 eV more negative than that of rutile as depicted in Fig. 2. In order to proceed the photocatalytic reaction effectively, the bottom level of CB has to be more negative than a reduction potential of  $A$  ( $A/A^{\cdot-}$ ), while the top level of VB has to be more positive than an oxidation potential of  $D$  ( $D^+/D$ ) as shown in Fig. 2.



**Figure 2.** Band gaps and band edge positions of some semiconductor photocatalysts

It should be also noted that the band levels usually shift with a change in pH ( $-0.059$  V/pH) for oxide materials. In addition to this pH dependence, surface impurities, adsorbed compounds, and the change to organic solvents would induce band shifts. For an example, the negative band shift is observed when water is replaced by organic solvents such as acetonitrile and alcohols [13]. The negative CB level is essential for the photoreductive hydrogenation reaction. From this point of view, ZnS and CdS having the negative CB level are effective candidates for the photocatalytic hydrogenation. However, these sulfides can be oxidized by  $h^+$  in the absence of an appropriate hole scavenger:  $CdS$  or  $ZnS + 2h^+ \rightarrow Cd^{2+}$  or  $Zn^{2+} + S$ , which is so called “photocorrosion” [8]. Thus, the choice of a suitable hole scavenger (solvent) is particularly important for hydrogenation using ZnS or CdS.

It is important to estimate a quantum yield (QY) in photocatalytic reactions. QY is defined as the number of events which occurs per photon absorbed by a photocatalyst as follows:

$$QY = \frac{(\text{number of reacted electrons or holes})}{(\text{number of absorbed photons})}$$

However, it is difficult to determine the real number of photons absorbed by a photocatalyst in a dispersed system because of light scattering by the photocatalyst powder. Therefore, in general, an apparent QY as described below is applied to the actual photocatalytic reactions.

$$\text{Apparent } QY = \frac{(\text{number of reacted electrons or holes})}{(\text{number of incident photons})}$$

The apparent QY is estimated to be smaller than the real QY because the number of absorbed photons is usually smaller than that of incident photons.

Loading of fine particles, usually nanometer size of noble metals (e.g. platinum (Pt) or silver (Ag) etc.) or metal oxide (nickel oxide (NiO) etc.), on the photocatalyst surface often improves the reaction efficiency as a co-catalyst due to the following reasons: (1) the particles enhance the charge separation between  $e^-$  and  $h^+$  and prevent the charge recombination, and (2) the particles act as effective reactive sites in the photocatalytic transformation processes. For an example, Pt fine particles loaded on photocatalyst greatly improve the chemical efficiency of hydrogen evolution from water or alcohol under irradiation.

### 3. Applications

#### 3.1. Hydrogenation of alkenes and alkynes

Photocatalytic hydrogenation of ethene and ethyne firstly reported by Boonstra and Mutsaers in 1975 [12]. Some hydrogenated products have been found upon the UV illumination (320 – 390 nm) of  $TiO_2$  in an atmosphere of ethene or ethyne. Main products from ethene were methane, ethane, propane, and *n*-butane, whereas, in the case of ethyne, the products were methane, ethene, ethane, and propane. In these reactions, the hydrogen source has been thought to be the surface Ti-OH group on  $TiO_2$ .

Anpo and co-workers investigated the photocatalytic hydrogenation of various alkenes and alkynes in the presence of water vapor upon  $TiO_2$  [14-17]. Major products on the UV illuminated  $TiO_2$  powders were the compounds formed by hydrogenation accompanied by C=C or C≡C bond fission [14, 15]. In contrast, a significant enhancement of hydrogenation products without the bond fission has been observed on the UV illuminated Pt-loaded  $TiO_2$  (Pt/ $TiO_2$ ) powders [16]. Especially, the Pt-loaded rutile  $TiO_2$  predominantly catalyzed the hydrogenation of propyne ( $CH_3C\equiv CH$ ) to afford  $C_3H_6$  and  $C_3H_8$  ( $C_3/C_2$  ratio = 5.60) as listed in Table 1. Anpo et al. further investigated the size effects on Pt/ $TiO_2$  particles in the photocatalytic hydrogenation of  $CH_3C\equiv CH$  with  $H_2O$  [17]. Quantum yields of the whole photoreactions became smaller with increasing the particle size of Pt/ $TiO_2$  (rutile), whereas selectivity of the hydrogenation products without vs. with the bond fission ( $C_3H_8/C_2H_6$ ) reversely became larger and reached at  $C_3H_8/C_2H_6 = 99$  upon the particle size of 200 nm.

Catalysts Type	Products ( $10^{-9}$ mol $m^{-2}$ $h^{-1}$ )					$C_3/C_2$ ratio
	$CH_4$	$C_2H_6$	$C_2H_4$	$C_3H_6$	$C_3H_8$	
$TiO_2$ (P25 <sup>a</sup> )	1.90	12.3	0.40	1.10	0.50	0.12
Pt <sup>b</sup> / $TiO_2$ (P25 <sup>a</sup> )	2.40	15.7	0.50	15.7	0.40	0.86
$TiO_2$ (rutile)	0.55	3.27	0.10	0.48	0.19	0.17
Pt <sup>b</sup> / $TiO_2$ (rutile)	0.22	1.60	0.23	10.3	1.10	5.60

<sup>a</sup> A composition ratio of rutile/anatase is ca. 1/4. <sup>b</sup> 4wt%

**Table 1.** The amount of products formed in the photocatalytic hydrogenation of  $CH_3C\equiv CH$  on the four type of  $TiO_2$  in the presence of water vapor at 300 K [16].

The hydrogenation of C-C multiple bonds of alkenes and alkynes was also examined in alcohols using Pt/TiO<sub>2</sub> powders by Yamataka et al. [18]. In this case, some saturated alkanes were produced in good yields (> 50% after 24 h), while the alcoholic solvents were concurrently oxidized to the corresponding carbonyl compounds. Baba et al. have synthesized bimetal-loaded TiO<sub>2</sub> such as Pd/TiO<sub>2</sub>/Ni or Pt/TiO<sub>2</sub>/Cu and applied those to the hydrogenation of ethene [19]. The hydrogenation to ethane was efficiently occurred upon the bimetal/TiO<sub>2</sub>, on which the role of the latter metals (Ni or Cu) was to suppress the hydrogen production as side reaction. Titanium-silicon (Ti/Si) binary oxides were prepared and utilized for the photocatalytic hydrogenation of alkenes and alkynes with H<sub>2</sub>O by Anpo's group [20-22]. The reactivity and selectivity for the hydrogenation of CH<sub>3</sub>C≡CH were investigated as a function of the Ti content [21, 22]. It was found that the hydrogenation with bond fission producing C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub> was predominant in regions of low Ti content, whereas the hydrogenation yielding C<sub>3</sub>H<sub>6</sub> proceeded in regions of high Ti content. They have revealed that tetrahedrally coordinated titanium oxide species played a significant role in the efficient photoreaction with a high selectivity for the hydrogenation with the bond fission, while the catalysts involving the aggregated and octahedrally coordinated titanium dioxide species showed a high selectivity for the hydrogenation producing C<sub>3</sub>H<sub>6</sub>, being similar to reaction using the powdered TiO<sub>2</sub> catalysts. Molybdenum oxide or sulfide complexes supported on TiO<sub>2</sub> were developed by Kunts and applied to the photocatalytic hydrogenation of ethyne [23, 24]. The sulfur systems were somewhat more efficient in the hydrogenation, and also favored the 2 electron-transferred product ethene rather than the 4 electron-transferred product ethane.

Yanagida et al. reported that visible light response CdS nanocrystallites (2 – 5 nm) catalyzed the efficient hydrogenation of electron-deficient alkenes with triethylamine (TEA) (Table 2) [25]. This reaction is the first example of visible light induced hydrogenation of alkenes on semiconductor particles. The hydrogenation (two electron reduction) was always accompanied with *cis-trans* isomerization (one electron reduction /oxidation process). The yield of the hydrogenation becomes favorable with increasing light intensity [26]. TEA was used for a sacrificial electron donor, in which the oxidation reaction proceeded as follows: Et<sub>3</sub>N + H<sub>2</sub>O + 2h<sup>+</sup> → Et<sub>2</sub>NH + CH<sub>3</sub>CHO + 2H<sup>+</sup>.

$\begin{array}{c} \text{R}^1 \quad \text{R}^2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \quad \text{or} \quad \begin{array}{c} \text{R}^1 \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{R}^2 \end{array} + 2\text{H}^+ + 2\text{e}^- \xrightarrow[\text{TEA in MeOH}]{\text{CdS, } > 400 \text{ nm}} \begin{array}{c} \text{R}^1 \quad \text{R}^2 \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$		Time / h	Conversion / %	Yield / %	-E <sub>red</sub> <sup>a</sup> / V
CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub> ( <i>cis</i> )	2	100	70	1.56
CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub> ( <i>trans</i> )	2	100	60	1.60
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	CN ( <i>cis</i> )	3	70	47	1.75
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	CN ( <i>trans</i> )	3	68	41	1.73
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> CH <sub>3</sub> ( <i>cis</i> )	3	100	76	1.75
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	CO <sub>2</sub> CH <sub>3</sub> ( <i>trans</i> )	3	100	92	1.75
C <sub>6</sub> H <sub>5</sub>	CO <sub>2</sub> CH <sub>3</sub> ( <i>trans</i> )	3	10	trace	1.98

<sup>a</sup> Polarographic half-wave reduction potential vs. SCE in MeOH.

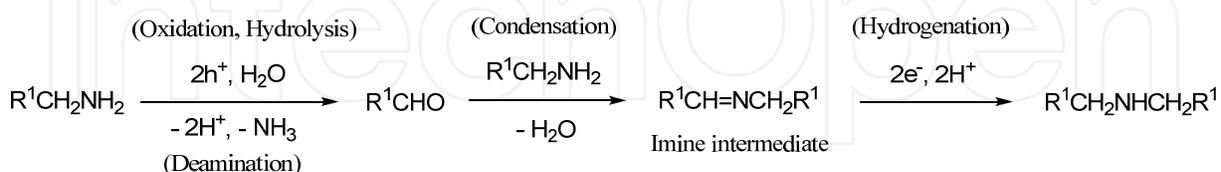
**Table 2.** CdS-catalyzed photohydrogenation of alkenes with triethylamine in MeOH [25].

### 3.2. Hydrogenation of imine, azo, and azide compounds

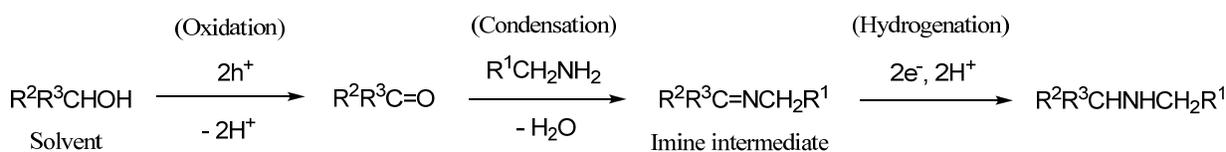
Hydrogenation of the C=N bond of imine intermediates upon the Pt/TiO<sub>2</sub> and CdS photocatalysts was observed during some inter- or intramolecular deaminocondensations in one-pot reaction systems as reported by Ohtani and co-workers [27, 28]. Fig. 3 illustrates the photocatalytic transformation of primary amine to symmetrical or asymmetrical secondary amines via the photocatalytic deaminocondensation in water or alcohols. In water [27], a primary amine was firstly oxidized by two holes to form an imine (R<sup>1</sup>CH=NH) followed by hydrolysis to give a corresponding aldehyde (R<sup>1</sup>CHO). Next, the aldehyde was condensed with another amine to yield the imine intermediate (R<sup>1</sup>CH=NCH<sub>2</sub>R<sup>1</sup>). Finally, the imine was photocatalytically hydrogenated to produce the symmetrical secondary amine (R<sup>1</sup>CH<sub>2</sub>NHCH<sub>2</sub>R<sup>1</sup>). On the other hand, in alcoholic solvent [28], the alcohol molecule (sacrificial hole scavenger) was primarily oxidized by two holes to afford the corresponding carbonyl compound (R<sup>2</sup>R<sup>3</sup>C=O) which was also condensed with amine to yield the imine intermediate (R<sup>2</sup>R<sup>3</sup>C=NCH<sub>2</sub>R<sup>1</sup>). The imine was further hydrogenated to form the asymmetrical secondary amine (R<sup>2</sup>R<sup>3</sup>CHNHCH<sub>2</sub>R<sup>1</sup>). This mechanistic principle has been used for several inter- or intramolecular reaction systems as depicted in Scheme 1. Furthermore, photocatalytic deaminocyclization of L-lysine to pipercolinic acid was examined using TiO<sub>2</sub> and CdS, and concluded that these two photocatalysts exhibited the different stereochemistry [29, 30].

Kisch et al. found that photocatalytic hydrogenation of azobenzene to hydrazobenzene on ZnS or CdS proceeded as a side reaction of a photocatalyzed addition of 3,4-dihydropyran to azobenzene giving 1-(3,4-Dihydro-2H-pyran-4-yl)-1,2-diphenylhydrazine (DPDH) (Scheme 2) [8, 31]. The formation of the hydrazobenzene was strongly favored when Pt-loaded ZnS or Pt-loaded CdS was used as the photocatalyst. This would be caused by the two electron-transfer process preferentially occurred on the platinum fine particles.

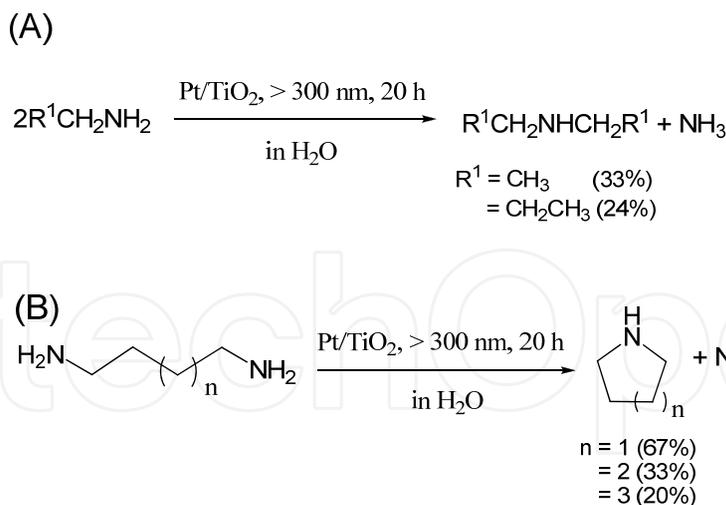
(A) in water



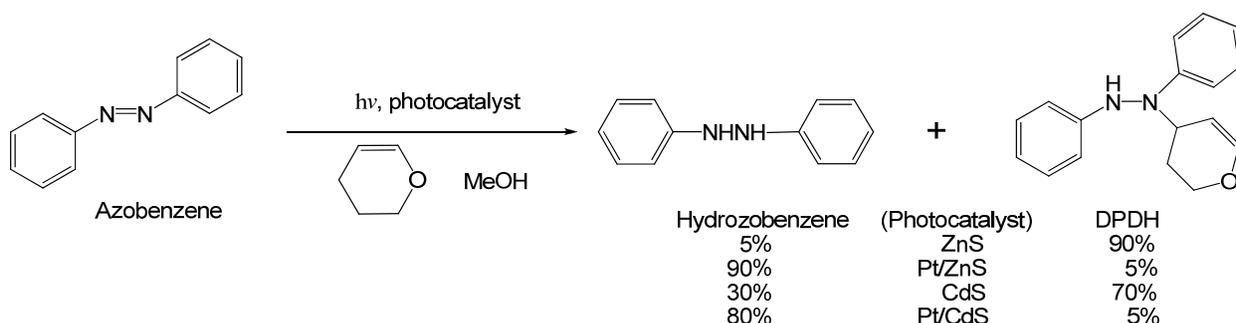
(B) in alcohol



**Figure 3.** Deaminocondensation reactions in one pot system containing hydrogenation process.



**Scheme 1.** Inter- (A) or intramolecular (B) deaminocondensation reactions [27].



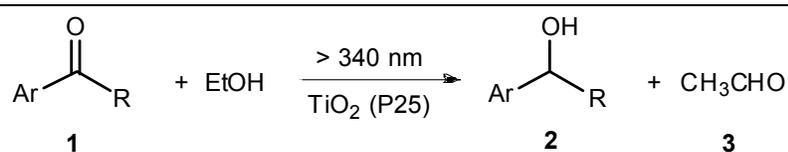
**Scheme 2.** Pt-loading effect on photocatalytic hydrogenation and addition reactions upon ZnS or CdS photocatalysts [8, 31].

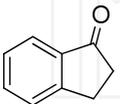
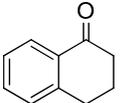
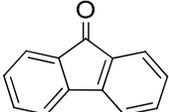
Photocatalytic hydrogenation of aromatic azides ( $Ar-N_3$ ) to amines upon CdS and cadmium selenide (CdSe) was examined by Warrier et al. [32]. The wide scope of the reaction was confirmed with compounds containing electron-withdrawing ( $-NO_2$ ,  $COOR$ ,  $COR$ ) and electron-donating groups ( $-OMe$ ,  $-R$ ,  $-Cl$ ) at the para-, meta-, and ortho-positions. These reactions took place with high quantum yields (near 0.5). Sodium formate was used as electron donor which was oxidized to  $CO_2$  during the reaction.

### 3.3. Hydrogenation of carbonyl compounds

Aldehydes and ketones are two classes of compounds that possess a reactive carbonyl group. The first report on photocatalytic hydrogenation of carbonyl compound is, to our knowledge, the hydrogenation of pyruvate to lactate under irradiation of aqueous suspension of  $TiO_2$  reported by Cuendet and Grätzel in 1987 [33]. Later, Li and co-workers reported P25  $TiO_2$ -catalyzed hydrogenation of benzaldehyde forming benzylalcohol in ca. 80% yield [34]. This reaction was recently applied to a micro-reaction system by Matsushita et al. [35, 36]. Kohtani et al. recently demonstrated that the P25  $TiO_2$  powder exhibited the excellent photocatalytic activity to hydrogenate several aromatic ketones into corresponding secondary alcohols under the combination of UV light irradiation and deaerated conditions

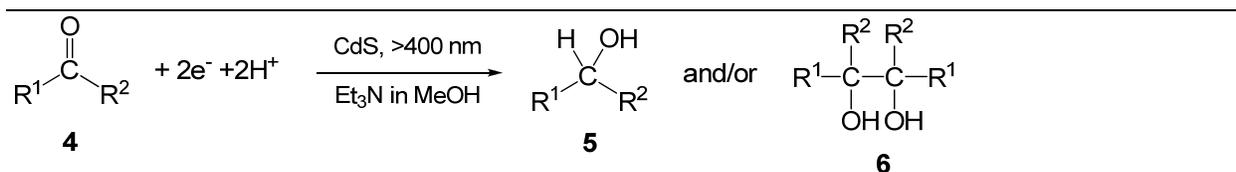




Substrates (1)		Time (h)	Conversion (%)	Yield of 2 (%)	Yield of 3 (%)	$-E_{\text{red}}$ (V) <sup>b</sup>
Ar	R					
C <sub>6</sub> H <sub>5</sub>	H	1	100	76±2	57	1.99
C <sub>6</sub> H <sub>5</sub>	Me	4	100	97±2	>99	2.13
C <sub>6</sub> H <sub>5</sub>	Et	8	91	87	>99	2.18
C <sub>6</sub> H <sub>5</sub>	<i>i</i> -Pr	8	24	25	32	2.21
C <sub>6</sub> H <sub>5</sub>	<i>t</i> -Bu	8	17	7	42	2.24
C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	8	70	63	10	1.59
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	4	82	78	97	1.83
2-MeC <sub>6</sub> H <sub>4</sub>	Me	8	66	63	84	2.16
4-MeC <sub>6</sub> H <sub>4</sub>	Me	8	100	>99	>99	2.15
2-FC <sub>6</sub> H <sub>4</sub>	Me	3	100	99	>99	1.86
3-FC <sub>6</sub> H <sub>4</sub>	Me	3	100	97	>99	2.04
4-FC <sub>6</sub> H <sub>4</sub>	Me	4	100	>99	>99	2.15
2,6-F <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Me	5	100	96	94	-
C <sub>6</sub> F <sub>5</sub>	Me	2	100	>99	>99	1.83
1-C <sub>10</sub> H <sub>7</sub>	H	1	95	76±3	77	1.66
1-C <sub>10</sub> H <sub>7</sub>	Me	10	100	>99	93	1.86
2-C <sub>10</sub> H <sub>7</sub>	H	1	94	32±7	93	1.70
2-C <sub>10</sub> H <sub>7</sub>	Me	5	100	94±4	>99	1.73
		8	100	>99	>99	2.06
		8	100	91	>99	-
		2	82	81	98	1.42

<sup>a</sup> Carried out for a mixture of the substrate **1** (3 mmol) and the P25 TiO<sub>2</sub> (0.1 g) in deaerated EtOH (30 cm<sup>3</sup>) under UV irradiation (>340 nm) at 32 °C. <sup>b</sup> Reduction potential vs. SCE in CH<sub>3</sub>CN containing Bu<sub>4</sub>NClO<sub>4</sub> electrolyte.

**Table 3.** Photocatalytic hydrogenation of aromatic carbonyl compounds on P25 TiO<sub>2</sub> [37].<sup>a</sup>

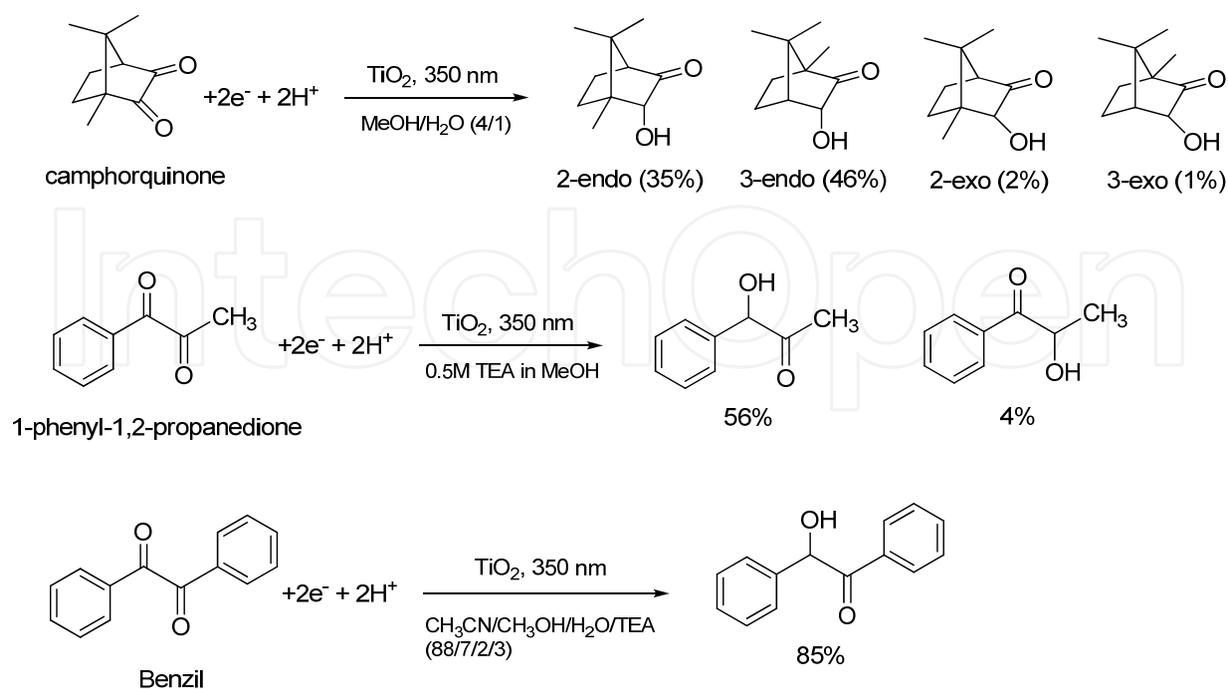


Substrates (4)		Time (h)	Conversion of 4 (%)	Yield of 5 (%)	Yield of 6 (%)	$-E_{\text{red}}$ (V) <sup>a</sup>
R <sup>1</sup>	R <sup>2</sup>					
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	2	100	95	0	1.17
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	3	98	70	12	1.32
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	3	98	90	4	1.35
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	3	100	95	5	1.55
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	3	97	33	56	1.56
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	3	52	15	40	1.56
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	3	10	trace	80	2.00

<sup>a</sup> Polarographic half-wave reduction potential vs. SCE in MeOH.

**Table 4.** Photocatalytic hydrogenation of aromatic ketones on nanocrystallized CdS [25].

1,2-Diketones such as camphorquinone, 1-phenyl-1,2-propanedione, and benzil were hydrogenated to the corresponding  $\alpha$ -hydroxyketones in moderate to good yields on the UV-irradiated P25 TiO<sub>2</sub> as shown in Scheme 4 [41, 42]. The yields and stereoselectivities were increased in the presence of water or TEA as a sacrificial electron donor in methanol solvent. The endo-hydroxycamphors were formed much more favorably than the exo-products, though there was little selectivity between 2 and 3 positions.



**Scheme 4.** Photocatalytic hydrogenations of diketone compounds upon the P25 TiO<sub>2</sub> powder.

### 3.4. Hydrogenation of carbon dioxide

With increasing concerns about rising atmospheric CO<sub>2</sub> concentration, the need for research to utilize CO<sub>2</sub> in chemical synthesis has been increased greatly [43]. Therefore, the photocatalytic hydrogenation of CO<sub>2</sub> upon semiconductor powders has received much attention [9-11, 44-56]. Among the earliest studies on the photocatalytic hydrogenation of CO<sub>2</sub>, Inoue et al. examined a wide range of semiconductors (WO<sub>3</sub>, TiO<sub>2</sub>, ZnO, CdS, GaP, and SiC in 200 – 400 mesh) in aqueous solution [44]. The results indicated that CO<sub>2</sub> was reduced to HCOOH, HCHO, and CH<sub>3</sub>OH, and the product yields correlated to the position of the CB level of the semiconductors. In the case of WO<sub>3</sub>, since the CB level was insufficiently negative to reduce CO<sub>2</sub>, no reduction products were observed. In contrast, SiC having the most negative CB level gave the highest yields. Later, Henglein and Gutiérrez reported that high quantum yield of 0.20 was achieved in the hydrogenation of CO<sub>2</sub> to formate using ZnS colloidal suspension under UV light irradiation [45]. Here, the solvent was a mixture of water and ethanol, or 2-propanol as the hole scavenger. After the earliest works, a great deal of effort has been devoted to studying the photocatalytic reduction of CO<sub>2</sub>. Most of works are summarized in recent reviews [9-11], in which the use of TiO<sub>2</sub>, SrTiO<sub>3</sub>, ZrO, ZnS, or CdS is reported. Recently, visible-light-driven new materials were developed and applied to the photocatalytic reduction of CO<sub>2</sub> under visible light irradiation: for examples, InTaO<sub>4</sub> [46], LaCoO<sub>3</sub> [47], BiVO<sub>4</sub> [48], ZnGaO<sub>4</sub> [49], Zn<sub>2</sub>GeO<sub>4</sub> [50, 51], Bi<sub>2</sub>WO<sub>6</sub> [52] etc.

The photocatalytic reduction of CO<sub>2</sub> on semiconductor powders gives several reduction products such as CO, HCOOH, HCHO, CH<sub>3</sub>OH, CH<sub>4</sub>, and various hydrocarbons. Among those, methanol is the most valuable product because it can be directly used as a fuel or a building block. High efficiency and selectivity in the preparation of methanol were obtained by the use of Ti-oxide/Y-zeolite catalysts containing highly dispersed tetrahedral titanium oxide species under UV irradiation [53, 54]. The charge-transfer excited state of these species played an important role in the selectivity for producing CH<sub>3</sub>OH, in contrast to the different selectivity giving CH<sub>4</sub> on bulk TiO<sub>2</sub> photocatalyst. Ti-incorporated mesoporous silica also exhibited high activity in the photoreduction of CO<sub>2</sub> with water to generate CH<sub>3</sub>OH and CH<sub>4</sub> under UV irradiation [55]. Methanol was also selectively produced by employing CaFe<sub>2</sub>O<sub>4</sub> [56] and NiO-loaded InTaO<sub>4</sub> [47] under visible light irradiation.

### 3.5. Hydrogenation of Nitrate and nitrite ions, and nitroaromatics

The use of artificial fertilizers in agriculture has caused a great deal of concern regarding water pollution induced by production of nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) ions from the fertilizers [57]. Therefore, chemical processes for elimination or hydrogenation of NO<sub>3</sub><sup>-</sup> ions have been extensively studied photocatalytically. TiO<sub>2</sub> photocatalyst has been used for the hydrogenation of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions to ammonia [58-60]. Other photocatalysts such as SrTiO<sub>3</sub> [61], K<sub>4</sub>NbO<sub>17</sub> [61], tantalate oxides (K<sub>3</sub>Ta<sub>3</sub>Si<sub>2</sub>O<sub>13</sub>, BaTa<sub>2</sub>O<sub>6</sub>, KTaO<sub>3</sub>, NaTaO<sub>3</sub>) [62], and ZnS [63], have also been reported as active photocatalysts for the hydrogenation of nitrate ions under UV light irradiation. It is worth noting that Kudo et al. developed a 0.1% nickel doped ZnS (Zn<sub>0.999</sub>Ni<sub>0.001</sub>S) photocatalyst to extend the photocatalytic response of ZnS

toward visible region [64], and applied it into the reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  ions under visible light irradiation [65]. The amounts of products and electrons consumed in the reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are listed in Table 5. The ratios of the amounts of  $\text{NH}_3/\text{NO}_2^-$  and  $\text{NH}_3/\text{N}_2$  increased in the presence of the platinum cocatalyst, indicating that selectivity for the  $\text{NH}_3$  production was improved by the Pt loading on  $\text{Zn}_{0.999}\text{Ni}_{0.001}\text{S}$ . More recently, Yamauchi and co-workers reported highly selective ammonia synthesis from nitrate with photocatalytically generated hydrogen on CuPd nanoalloys loaded on  $\text{TiO}_2$ , on which ammonia was selectively produced up to 78% yield with hydrogen evolution under UV light irradiation [66].

Catalysts Type	Reactant (initial conc./ molL <sup>-1</sup> )	Amounts of products (electron consumed)/ $\mu\text{mol}$			
		$\text{H}_2^b$	$\text{NO}_2^-$	$\text{NH}_3$	$\text{N}_2$
non-loaded	no $\text{NO}_3^-$ nor $\text{NO}_2^-$ (0)	214 (428)	(-)	(-)	(-)
non-loaded	$\text{NO}_3^-$ (1.0)	60 (120)	250 (500) <sup>c</sup>	21 (168) <sup>d</sup>	2.7 (27) <sup>e</sup>
1wt% Pt-loaded	$\text{NO}_3^-$ (1.0)	212 (424)	14 (28) <sup>c</sup>	11 (88) <sup>d</sup>	0.79 (7.9) <sup>e</sup>
non-loaded	$\text{NO}_2^-$ (0.01)	37 (74)	(-)	41 (246) <sup>f</sup>	2.4 (14) <sup>g</sup>
1wt% Pt-loaded	$\text{NO}_2^-$ (0.01)	96 (192)	(-)	65 (390) <sup>f</sup>	9.5 (57) <sup>g</sup>

<sup>a</sup> Carried out for a mixture of reactant ( $\text{NO}_3^-$  or  $\text{NO}_2^-$ ) and photocatalyst powder (0.5 g) in aqueous  $\text{CH}_3\text{OH}$  solution (6.25 vol%) under visible light irradiation ( $>420$  nm) for 20 h.

<sup>b</sup> A by-product from the reduction of water:  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ .

<sup>c</sup>  $\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$ . <sup>d</sup>  $\text{NO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$ . <sup>e</sup>  $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$ . <sup>f</sup>  $\text{NO}_2^- + 7\text{H}^+ + 6\text{e}^- \rightarrow \text{NH}_3 + 2\text{H}_2\text{O}$ . <sup>g</sup>  $2\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$ .

**Table 5.** Reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  on  $\text{Zn}_{0.999}\text{Ni}_{0.001}\text{S}$  photocatalysts [65].<sup>a</sup>

Several organic nitroaromatics can be easily hydrogenated to afford corresponding amino compounds in the presence of sacrificial hole scavenger upon the UV irradiated  $\text{TiO}_2$  as firstly reported by Li and co-workers in 1993 [67]. Since then, the photocatalytic hydrogenation of nitro compounds using some kinds of semiconductor photocatalysts was extensively studied by a number of researchers. The hydrogenation reactions proceeded almost quantitatively. The details are summarized in recent reviews [9-11]. Recent progress in this research has been directed toward the development of visible light response photocatalysts such as nitrogen-doped  $\text{TiO}_2$  [68] and dye-sensitized  $\text{TiO}_2$  loaded with transition metal nanoparticles [69].

#### 4. Advantages and disadvantages using this method

Compared to the conventional hydrogenation methods as mentioned in other Chapters, the photocatalytic hydrogenation on semiconductor particles has some great advantages: (1) The most important merit is that particular reducing agents (e.g.  $\text{H}_2$  gas etc.) are not necessary in this method. In most case, the reductants are conventional solvents such as water, alcohols, and amines which concurrently act as hole scavengers. Therefore, this method allows us to avoid both the use of harmful and dangerous chemical reagents and the emission of harmful waste. (2) The reactions mostly proceed under mild conditions, e.g.

under ordinary temperature and pressure, and therefore are safety. (3) In the case of  $\text{TiO}_2$  or other stable metal oxide photocatalysts, the materials are chemically stable, easily removal, and reusable. These three significant advantages imply that this method holds great promise to become an alternative “green” synthetic method.

On the other hand, a disadvantage of this method is to be unsuitable for a large-scale synthesis, because the rate of surface reaction on photocatalysts under irradiation are limited by electron-hole recombination, smaller surface area, lesser adsorptive and diffusive properties of substrates compared to those of the conventional catalysis. Therefore, up to now, scaling-up of the semiconductor photocatalysis has been successfully applied only to wastewater treatment, in which solar photocatalytic degradation of water contaminants, persistent toxic compounds and cyanide etc., is carried out on low concentration of the contaminants [70, 71]. In contrast, highly chemoselective and stereoselective hydrogenations have been made on a pilot plant scale and even fewer are available commercially on a multi kg scale by the conventional heterogeneous or homogeneous hydrogenation methods [72].

## 5. Concluding remarks and future directions

The photocatalytic hydrogenation on semiconductor particles has developed as the highly efficient and selective reaction during the past three decades. For examples, the selective hydrogenations were reported for the reactions of  $\text{CH}_3\text{C}\equiv\text{CH}$  to  $\text{CH}_3\text{CH}=\text{CH}_2$  on  $\text{Pt}/\text{TiO}_2$  (rutile) [17], the aromatic ketones to the corresponding secondary alcohols on the P25  $\text{TiO}_2$  [37], the aliphatic ketones to the corresponding alcohols on the  $\text{ZnS}$  nano-crystallite [39], and nitroaromatics to the corresponding amino-compounds on  $\text{TiO}_2$  [67-69]. In addition, the selective formation of methanol from  $\text{CO}_2$  [53-56] and  $\text{NH}_3$  from  $\text{NO}_3^-$  [65, 66] has been received much attention to solve the environmental issues. Recent progress in the reductive hydrogenation has been directed toward the development of visible light response photocatalysts to utilize solar energy effectively [46-52, 65, 68, 69].

One of the most significant features of semiconductor photocatalysis is that we can utilize both oxidation and reduction in one-pot processes as mentioned in the deaminocondensation reactions [27-30]. The combination of redox reactions can afford several unique reactions, which are not achieved by conventional reaction techniques. Thus, the semiconductor photocatalysis is one of promising methods in fine chemical synthesis for high value pharmaceuticals etc. In order to achieve this method, development of highly stereoselective photocatalysis will be indispensable, although less known about such semiconductor photocatalysts so far. Therefore, particular attention should be directed toward the development of new enantioselective semiconductor catalyzed reactions in the future.

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