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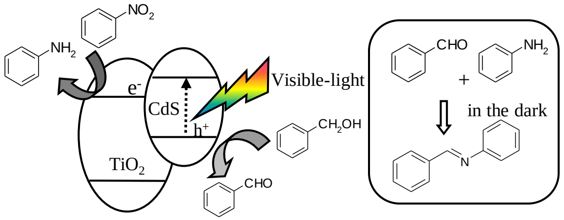
Photocatalyzed one-pot synthesis of imine from benzyl alcohol and nitrobenbzene on the CdS-TiO_2 under visible-light irradiation



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ARTICLE TYPE

One-pot synthesis of imine from benzyl alcohol and nitrobenzene on visible-light responsive CdS-TiO$_2$ photocatalysts

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The one-pot synthesis of imine (N-benzylideneaniline) from benzyl alcohol and nitrobenzene was studied on the CdS-TiO$_2$ photocatalyst under visible-light irradiation ($\lambda > 420$ nm) at 298 K. The photocatalytic activity strongly depends on the loadings of CdS on the TiO$_2$, and the preferable amount of CdS was 15 wt%. Photo-electrochemical investigations were also incorporated to demonstrate the reaction mechanism: the CdS is photosensitized by visible-light irradiation, and an effective hole-electron separation is generated in the hetero-junction between CdS and TiO$_2$. It was also confirmed that the photocatalytic oxidation of benzyl alcohol proceeds over the CdS surface, while the hydrogenative reduction of nitrobenzene into aminobenzene proceeds over the TiO$_2$ surface. Moreover, the production of imine proceeded efficiently by the successive condensation of benzaldehyde and aminobenzene on the catalyst surface under dark conditions.

Introduction

The design and development of an effective photocatalyst to address such energy and environmental needs[1-6] as H_2 production by water splitting, the degradation of volatile organic compounds (VOC), and organic syntheses is strongly desired. In particular, the development of visible-light sensitive photocatalyst has been the focus of much attention since solar irradiation is unlimited and ca. 50 % which reaches the earth's surface is visible light. These reactions are induced by photo-excitation of the catalyst to produce charge carriers (holes and electrons) which participate in the oxidation and reduction of the substrates, respectively.

The chemo-selective oxidation of organic compounds such as alcohols and amines into the corresponding carbonyl compounds and imines, respectively, is a fundamental but significant procedure with great potential in commercial applications[7, 8]. In particular, imines are important intermediates for the synthesis of pharmaceutical and agricultural chemicals[9], and they are utilized for the synthesis of secondary amines by hydrogenation[10], in cycloaddition reactions[11] and biologically active substances such as antibiotics[12].

The selective photocatalytic formation of imines by the aerobic coupling of amines[13-18] has been extensively studied not only on TiO$_2$[13, 14] and Au/TiO$_2$[15], but also on other semiconductive photocatalysts such as Nb_2O_5[16, 17] and C_3N_4[18] under UV and/or visible-light irradiation. These photocatalytic systems mainly have proceeded to form products at the oxidative sites, while H_2O and/or H_2O_2 are simultaneously formed as the O_2 reductive products. However, the oxidation of amines by O_2 sometimes causes over-oxidation of the products and/or side-products which could lead to catalyst deactivation.

Contrary to oxidation reactions, the hydrogenation of nitro-compounds is also an important procedure in the formation of amines. Recently, the photocatalytic reduction of nitrobenzene using TiO$_2$[19, 20] or Au/TiO$_2$[21] photocatalysts in the presence of such sacrificial reagents as 2-propanol and oxalic acid has been reported. It was confirmed that nitrobenzene is reduced into aminobenzene with 6 electrons at the reductive sites, while 2-propanol and oxalic acid are oxidized into acetone and CO$_2$, respectively, at the oxidative sites.

One-pot synthesis has been an efficient strategy in order to improve successive chemical reactions in just one reactor. This system can avoid the relatively long separation and purification processes of the intermediates. Several one-pot photocatalytic syntheses of amines, imines, benzimidazoles, indazoles and azobenzenes in alcoholic suspensions of TiO$_2$ or CdS under UV-light irradiation have also been previously reported[22-24].

Along these lines, we have developed an efficient photocatalytic system for the one-pot synthesis of imines from alcohols and nitro-compounds under visible light irradiation. This catalytic system consists of three steps: 1) the oxidation of alcohol into aldehyde; 2) reduction of nitro-compounds into amine; and 3) successive condensation of aldehyde and amine to form imine. It is, thus, desirable that both photo-induced oxidative and reductive products participate in further reactions to form more useful products.

Recently, the Pd-deposited CdS-TiO$_2$ photocatalyst was found to exhibit the selective dehydrogenation of aromatic alcohols into corresponding carbonyl compounds together with H_2 under visible-light irradiation ($\lambda > 420$ nm) at 298 K[25]. It was clearly demonstrated that the charge carriers (holes and electrons) induced on the CdS-TiO$_2$ led to effective photocatalytic reactions under visible-light irradiation. This photocatalytic system has the advantage of preventing photo-dissociation of the CdS photocatalyst in the absence of O_2.

In this study, we have investigated the one-pot synthesis of imine from benzyl alcohol and nitrobenzene in an acetonitrile suspension with the CdS-TiO$_2$ photocatalyst and without the use of a precious metal co-catalyst under visible light irradiation ($\lambda >$ 420 nm) at 298 K. Here, we have studied the reaction mechanism through a combination of photo-electrochemical measurements.

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Experimental

Preparation of the photocatalysts

Commercially available bulk TiO_2 (320 m^2 g^{-1}, ST-01, Ishihara Co., Ltd.) and CdS (Sigma Aldrich Japan), benzyl alcohol, nitrobenzene, aminobenzene and N-benzylideneaniline, $Cd(NO_3)_2$ and Na_2S (Wako Pure Chemical Industries, Ltd.) were used as received.

The CdS-supported TiO_2 (CdS-TiO_2) was prepared by impregnation of TiO_2 with aq. $Cd(NO_3)_2$ at the desired concentrations. The precursors were dipped in aq. Na_2S involving the same amounts of S^{2-} ions with Cd^{2+} ions at 298 K for 48 h, followed by washing with water/acetonitrile several times and dried under vacuum for 24 h. The obtained sample was referred to as CdS (x wt%)-TiO_2, x: wt% as CdS.

Photocatalytic reactions

An acetonitrile solution (5.0 mL) of benzyl alcohol (150 μmol) and nitrobenzene (50 μmol) suspended with the photocatalyst (10 mg) was introduced in a pyrex cell under purging with N_2. It was then irradiated by blue LED lamps adjusted to 25000 Lux (λ_{max} = 460 nm, ca. 10 mW/cm^2). After the reactions, the catalysts were immediately separated from the suspension by filtration through a 0.20-μm membrane filter (Dismic-25, Advantec). The solution was then analyzed by gas chromatography: GC-FID (Shimadzu GC-14A, capillary column: INERTCAP 1701).

Measurements of apparent quantum yields (AQY)

The AQY was measured in a quartz cell involving an acetonitrile solution (2 mL) of benzyl alcohol (150 μmol) and nitrobenzene (50 μmol) suspended with CdS(15 wt%)-TiO_2 (10 mg) using a 100 W Xenon lamp (Lax Cute II, Asahi Spectra Co., Ltd.) through appropriate band path filters with a FWHM of 10±2 nm. The AQY at each centered wavelength of light was calculated using the following equation (1), where the products represent the total amounts of benzaldehyde and N-benzylideneaniline:

$$\text{AQY [\%]} = \frac{\text{(amounts of product formed)}}{\text{(amounts of photons irradiated)}} \times 100 \qquad \text{(eq. 1)}$$

It was assumed that benzyl alcohol is converted into benzaldehyde through two electron-transfers by one photon due to the current doubling effect[26]. The flux of incident photons was adjusted within a range of 7.61×10^{18} ~ 1.10×10^{19} photons·h^{-1}, measured using a power-meter (Ophir, ORION/PD).

Characterizations

UV-Vis spectroscopic measurements of the samples were carried out in diffused reflectance mode using a UV-Vis spectrophotometer (UV-3100PC, Shimadzu). Powder X-ray diffraction (XRD) patterns were obtained with a RIGAKU RINT2000 diffractometer using Cu K_α radiation (λ=1.5417 Å). The amounts of Cd leached in the solution were analyzed by a multi-type ICP emission spectrometer (ICPE-9000, Shimadzu). The elemental composition of the photocatalysts was characterized by scanning electron microscope (SEM) with energy dispersive X-ray (EDX) spectroscopy (JSM-6610, JEOL).

Photo-electrochemical measurements

The electrolysis cells separated by Nafion® (Aldrich) were filled with two types of electrolytes. The acetonitrile solutions involve 0.1 M $LiClO_4$ with 30 mM benzyl alcohol (A) and 10 mM nitrobenzene (B), as shown in Fig. 1. Two electrodes were connected to a Potentiostat/Galvanostat (HABF5001, HOKUTO DENKO). The TiO_2 film was prepared as follows: TiO_2 powder (2.85 g of Degussa P-25 and 0.15 g of ST-01) was well-dispersed in 5 mL of aq. HNO_3 (pH 3) involving 0.3 g of polyethyleneglycol (H_w = 20000) and 0.3 mL of Toriton X-405, and the paste was then spread onto an ITO-glass electrode (10 Ω·cm^{-2}) by spin coating, followed by heat-treatment at 673 K for 1h in air. This process was repeated twice.

A $Cd(OH)_2$ film was electrochemically deposited onto the ITO at -1.0 V vs. Ag/AgCl with an electro-charge of 0.2 C·cm^{-2}, followed by the reaction with 0.1 M Na_2S for 1 h at 298 K to form CdS. Details on the characterization of the CdS films have been previously reported[27].

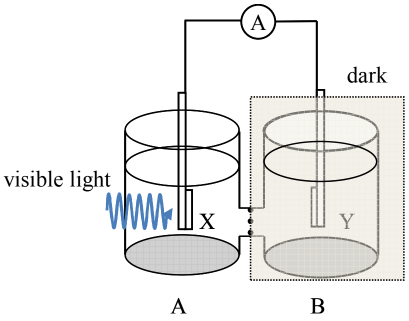

Figure 1 Schematic illustration of the separated cells; the X electrode is illuminated by visible-light, while Y is placed under dark conditions.

Results and discussions

The photocatalytic reaction of benzyl alcohol and nitrobenzene was performed on CdS-TiO_2 under visible light irradiation. It was confirmed that the reaction does not take place under visible light without the photocatalyst nor with the photocatalyst but without irradiation.

Figure 2 shows the time profile for the synthesis of imine from benzyl alcohol and nitrobenzene on the CdS(15 wt%)-TiO_2 photocatalyst under visible light irradiation (λ > 420 nm). A decrease in the amount of benzyl alcohol and nitrobenzene was observed with an increase in the irradiation time, while an increase in the amount of benzaldehyde and aminobenzene was observed for up to 6 h. A decrease in the amount of benzaldehyde and aminobenzene was then observed, while the successive condensation of benzaldehyde and aminobenzene led to the

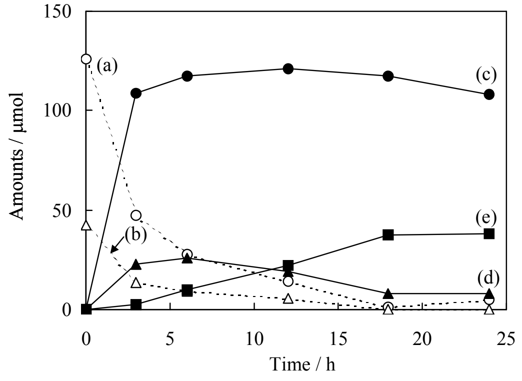

Figure 2 Time profile for the photocatalytic reaction of nitrobenzene and benzyl alcohol on the CdS (15 wt%)-TiO_2 under visible-light irradiation. (a) benzyl alcohol, (b) nitrobenzene, (c) benzaldehyde, (d) aminobenzene, (e) N-benzylideneaniline.

formation of N-benzylideneaniline. The carbon and nitrogen mass-balance were almost stoichiometric within 5% for each reaction time. This reaction exhibited a turnover number (TON), *i.e.*, the total number of photo-formed benzaldehyde and N-benzylideneaniline per Cd atom for 24 h was determined to be ca. 14, indicating that this reaction system takes place photocatalytically. It should be noted that the concentration of Cd in the solution after the reaction was below the detection limit for ICP analysis (< 0.01 ppm), suggesting that the anodic photo-corrosion of CdS was successfully suppressed.

The dependence of the amount of CdS loaded on TiO_2 upon photocatalytic activity is shown in Fig. 3. Only traceable N-benzylideneaniline was formed when both TiO_2 and CdS by themselves were applied as the photocatalyst. However, it was observed that the photocatalytic activity increases with an increase in the amount of CdS up to 15 wt% and then decreases. These results indicate that the synergetic effects between TiO_2 and CdS play significant roles in the enhancement of the activity.

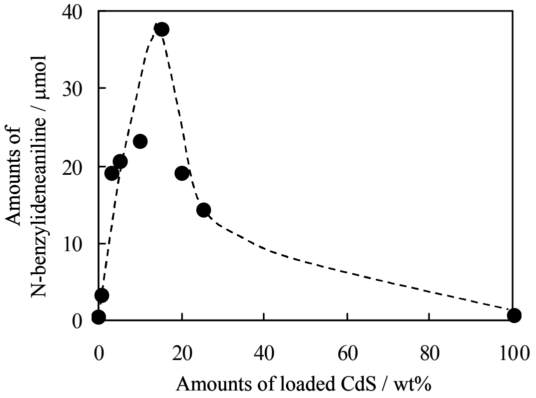

Figure 3 Effect of the amount of CdS (x wt%) on the photo-formed N-benzylideneaniline. Reaction conditions: photocatalyst (10 mg), nitrobenzene (50 μmol), benzyl alcohol (150 μmol), blue LED (λ_{max} = 460 nm, 25000 lux), reaction time (24 h).

In order to understand the role of the components of the photocatalyst, various examinations were carried out under visible light irradiation and the results are listed in Table 1. It was observed that the TiO_2 exhibited the formation of small amounts of benzaldehyde and aminobenzene, but only trace amounts of imine (Run 1), suggesting that the TiO_2 by itself does not exhibit significant photocatalytic reaction. On the other hand, CdS by itself showed photocatalytic activity for the formation of benzaldehyde and aminobenzene, while little formation of N-benzylideneaniline was observed (Runs 2, 3). Moreover, CdS (15 wt%)-TiO_2 was found to improve the activity, accompanied by the formation of N-benzylideneaniline (Run 4). It was also observed that the activity of the CdS(15 wt%)-supported SiO_2 was much lower than that of the CdS (15 wt%)-TiO_2 (Run 5). These results indicate that CdS works as the photo-sensitizer, and the TiO_2 surface plays a significant role in the enhancement of the activity for the production of N-benzylideneaniline.

Table 1. Reaction of benzyl alcohol and nitrobenzne on various photocatalysts under visible light irradiation.

Run	Photocatalyst[a]	Time / h	Amounts / μmol		
			Ph-CHO	Ph-NH_2	Ph-C=N-Ph
1	TiO_2	24	5.7	0.8	trace
2	CdS	12	51.3	10.0	trace
3	CdS	24	64.3	16.7	0.7
4	CdS(15 wt%)-TiO_2	12	121.2	19.2	22.1
5	CdS(15 wt%)-SiO_2[b]	12	16.8	1.8	trace

[a] Reaction conditions: catalyst (10 mg); benzyl alcohol (150 μmol), nitrobenzene (50 μmol) in acetonitrile (5 mL). [b] SiO_2 (390 $m^2 \cdot g^{-1}$, S5130-500G, Aldrich)

Table 2 shows the results of the condensation of benzaldehyde and aminobenzene under dark conditions. This reaction proceeds even in the absence of catalysts under dark conditions. The activity remarkably increases in the presence of the active surfaces of CdS, TiO_2 and CdS(15 wt%)-TiO_2. Therefore, the production of N-benzylideneaniline was confirmed to proceed efficiently by the successive condensation of the photo-produced benzaldehyde and aminobenzene on the catalyst surface under dark conditions. It should be noted that the photocatalytic activity for the synthesis of imine on the CdS surface is quite low, as shown in Table 1 (Runs 2, 3) in spite of the high activity for condensation on the CdS surface. This is probably due to the blocking effect of the active sites for condensation reactions by the reactants and/or intermediates during the reaction.

Table 2. Reactions of benzaldehyde and aminobenzene on various catalysts under dark conditions.

Run	Catalyst[a]	Time / h	Amounts / μmol
			N-benzylideneaniline
1	-	24	25.8
2	CdS	24	42.5
3	TiO_2	24	42.8
4	CdS(15 wt%)-TiO_2	24	43.4

[a] Reaction conditions: catalyst (10 mg); benzaldehyde (150 μmol), aminobenzene (50 μmol) in acetonitrile (5 mL).

The characterization of the CdS(15 wt%)-TiO_2 photocatalyst was performed by XRD, SEM-EDX and UV-Vis spectroscopies. The XRD patterns of TiO_2, CdS(15 wt%)-TiO_2 and CdS are shown in Fig. 4. CdS(15 wt%)-TiO_2 is observed to involve CdS with a cubic structure and TiO_2 with an anatase structure. By the Scherer equation, the crystal size of TiO_2 and CdS were estimated to be ca. 7.5 and 3.6 nm, respectively.

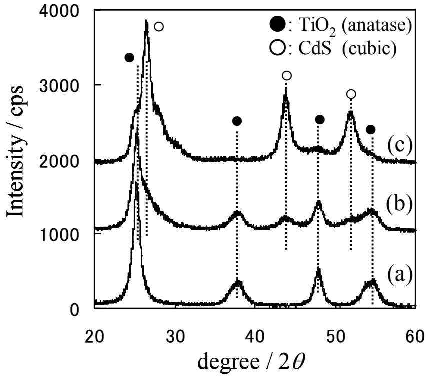

Figure 4 XRD patterns of (a) TiO_2, (b) CdS(15 wt%)-TiO_2 and (c) CdS.

Figure 5 [I] and [II] show the SEM photograph and distributions of Ti, O, Cd, and S elements obtained by EDX analysis, respectively, on CdS(15 wt%)-TiO_2. The red and white colors represent the high concentration of the corresponding elements in Fig. 5 [II]. It was observed that the elements of Cd and S are randomly dispersed at locations of low Ti and O concentrations, and the ratio of S/Cd was ca 1.0. These results indicate that stoichiometric but partially aggregated CdS species with an island structure is formed on the TiO_2 surface. Therefore, such reactants as benzyl alcohol and nitrobenzene can interact not only with the TiO_2 but also CdS surface on the CdS(15 wt%)-TiO_2 photocatalyst.

Figure 6 shows the UV-Vis spectra of CdS(15 wt%)-TiO_2 (a) together with the pure TiO_2 (b) and CdS (c). It was observed that the TiO_2 exhibits a direct band-gap excitation under UV-light irradiation. However, the CdS (15 wt%)-TiO_2 photocatalyst exhibits visible-light absorption above 400 nm almost identical to absorption of the pure CdS. It was observed that the absorption edges of all CdS-TiO_2 photocatalysts are identical. These results indicate that polycrystalline CdS is formed on the TiO_2. The relationship between the photocatalytic activity as apparent quantum yields (AQY) and the wavelength of the irradiated light was then examined in order to identify the photo-responsible center. The AQY at various wavelengths of irradiated light on CdS(15 wt%)-TiO_2 is also shown in Fig. 6. The AQY were determined as follows: 17.3% at 480 nm, 8.7% at 540 nm, and ca. 1.5% at 600 nm. The AQY plots form the action spectrum for the photocatalytic reaction on CdS(15 wt%)-TiO_2. These results show that the action spectrum is in good agreement with the photo-absorption of CdS(15 wt%)-TiO_2. It could, thus, be concluded that the CdS on the TiO_2 works as the photo-responsible center for the visible-light induced photocatalytic dehydrogenation of benzyl alcohol.

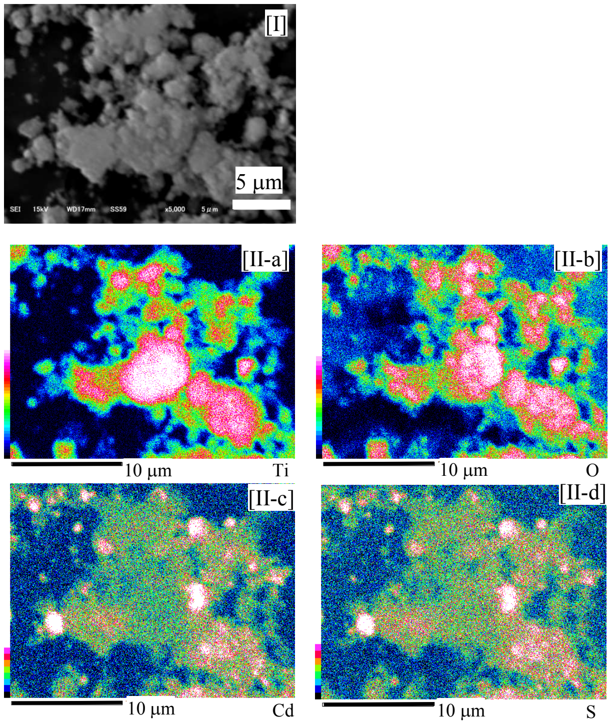

Figure 5 SEM image [I], and elemental mappings [II] (a) Ti, (b) O, (c) Cd and (d) S of the CdS (15 wt%)-TiO_2.

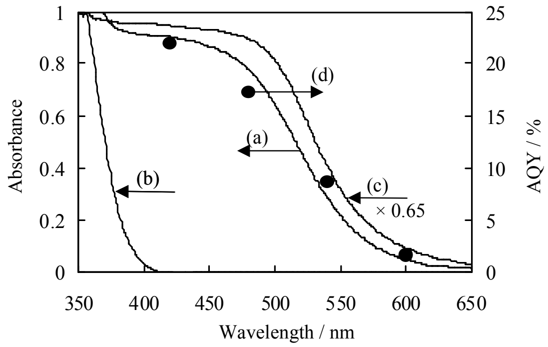

Figure 6 UV-Vis spectra of: (a) CdS(15 wt%)-TiO_2, (b) TiO_2, (c) CdS and (d) AQY plots for the formation of benzaldehyde and N-benzylideneaniline in total.

The photocatalytic activity for the reaction of (a) normal benzyl alcohol and (b) α, α-d_2 benzyl alcohol with nitrobenzene is shown in Fig. 7 [I]. It was observed that the photocatalytic activity of normal benzyl alcohol with nitrobenzene was much higher than that of α, α-d_2 benzyl alcohol. The reaction rate constants of k_H and k_D for (a) and (b), respectively, in Fig. 7 [I] have been evaluated from the first-order rate law in equation (2).

$$k\,t = \ln\left[\frac{a}{(a-x)}\right] \qquad \text{(eq. 2)}$$

Equation (2) shows that when ln [a / (a - x)] is plotted against t, the first-order reaction gives a straight line for slope k. Here, the amount of added benzyl alcohol and photo-formed products (benzaldehyde and N-benzylideneaniline in total) are defined as a and x, respectively. The reaction rate constants for normal benzyl alcohol and α, α-d_2 benzyl alcohol were roughly estimated to be 8.94×10^{-5} s^{-1} and 3.43×10^{-5} s^{-1} for (c) and (d), respectively (cf. Fig. 7 [II]). The ratio of the reaction rates (k_H/k_D) was, therefore, estimated to be ca. 2.6. The first order isotope effect shows that the C-D bond is cleaved more slowly than the C-H bond. It should be noted that the value of $k_{C\text{-}H}/\ k_{C\text{-}D}$ is theoretically ≈ 8 when the C-H bond is completely cleaved at the transitional state. Here, from the value of $k_{C\text{-}H}/\ k_{C\text{-}D}$ at ≈ 2.6, the kinetic isotope effect shows that an abstraction of the α-hydrogen atom from the

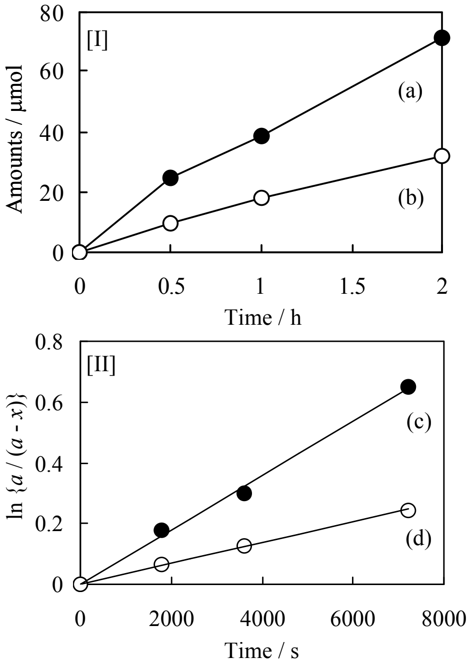

Figure 7 Time profile for the photocatalytic reaction of (a) normal benzyl alcohol and (b) α, α-d_2 benzyl alcohol with nitrobenzene on CdS(15 wt%)-TiO_2 under visible-light irradiation [I], and the plots for ln [a/(a-x)] against the time [II] for (c) normal benzyl alcohol and (d) α, α-d_2 benzyl alcohol.

-CH_2OH group is a rate-determining step while the C-H bond is partially left in the transitional state.

In order to understand the reaction mechanism for the photocatalytic reaction, a photo-electrochemical technique was incorporated. We fabricated the photo-electrochemical cell, *i.e.*, the electrodes X and Y participate in the oxidation of benzyl alcohol under visible-light irradiation, and the reduction of nitrobenzene under dark conditions, respectively, as shown in Fig. 1. It should be noted that the influence of the chemical bias can be ignored since the pH of the electrolytes A and B are 5.8 and 6.0, respectively. Several types of controlled experiments were carried out under no bias and the results are shown in Fig. 8. First, when the TiO_2 electrode for X, and TiO_2 or CdS for Y were used, they exhibited little photocurrent. These results indicate that TiO_2 in itself is not sensitized by visible-light irradiation. When the CdS electrodes for X and Y were used, respectively, it exhibited stable photocurrent (i). That is, CdS induces the photo-oxidation of benzyl alcohol at the X, while the photo-formed electrons reduce nitrobenzene at the Y. Moreover, when Y involved the TiO_2 film instead of CdS, the photocurrent (ii) was significantly enhanced five times higher than (i). This is because the conduction band of CdS is more cathodic than that of TiO_2[28], and the photo-induced electrons on the CdS electrode effectively transfer into the TiO_2.

When the uptakes in a mixture of benzyl alcohol and benzaldehyde (150 μmol for each) on CdS (15 wt%)-TiO_2 (10 mg) were investigated, the amount of benzaldehyde adsorbed on the photocatalyst was negligible compared to that of benzyl alcohol (ca. 30 μmol). These results indicate that the interaction between benzaldehyde and TiO_2 is fairly weak. Therefore, once benzaldehyde is produced by the oxidation of benzyl alcohol, it is immediately released into the bulk solution. This may be one of the reasons benzaldehyde is selectively formed and not oxidized further to benzoic acid or CO_2. Moreover, it was confirmed that photo-formed aminobenzene is rarely oxidized on the CdS(15 wt%)-TiO_2 surface in the absence of O_2 under visible-light irradiation. From these results, a possible mechanism for imine synthesis on the CdS-TiO_2 is shown in Fig. 9. The CdS is photosensitized under visible-light irradiation, and an effective hole-electron separation is generated in the hetero-junction between CdS and TiO_2. The photo-induced holes participate in the oxidation of three benzyl alcohol molecules into three benzaldehyde molecules. On the other hand, the reaction of 6 electrons left in the TiO_2 together with 6 protons with one nitrobenzene molecule will afford one aniline molecule on the TiO_2 surface since the reductive potential of nitrobenzene (+0.16 V vs. SHE) is more anodic than that of the conduction band (CB) of TiO_2 (-0.18 V vs. SHE)[28, 29]. These reactions consecutively proceed by way of the formation of a as a minor species only at the initial reaction time. Furthermore, N-benzylideneaniline is readily formed by the successive reaction of aminobenzene and benzaldehyde on the catalyst surface under dark conditions.

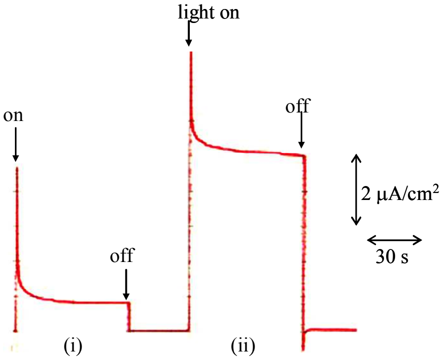

Figure 8 Photocurrent under zero bias on two types of configurated electrodes: (i) X: CdS, Y:CdS and (ii) X: CdS, Y: TiO_2, respectively

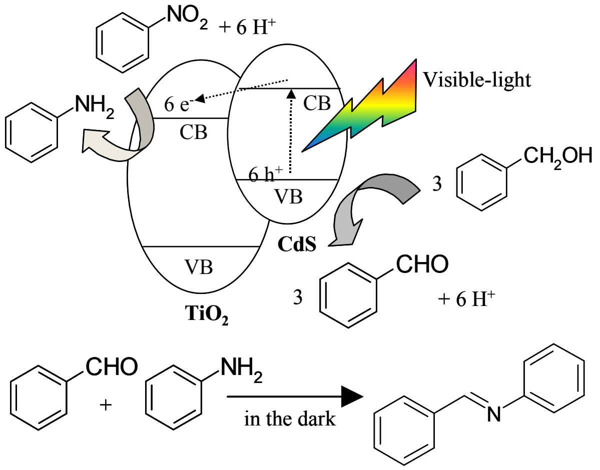

Figure 9 Schematics for the one-pot synthesis of imine from benzyl alcohol and nitrobenzene on the CdS-TiO_2 photocatalyst.

Conclusions

The photocatalytic synthesis of imine (N-benzylideneaniline) from benzyl alcohol and nitrobenzene was successfully demonstrated on the CdS-TiO_2 photocatalyst by a one-pot method at 298 K under visible-light irradiation. The photocatalytic activity strongly depends on the loadings of CdS on the TiO_2, and the amount of CdS was optimized to be 15 wt%. CdS particles with an island structure were found to form on the TiO_2. Photo-electrochemical investigations were also incorporated to demonstrate the reaction mechanism, *i.e.*, that the photo-oxidation of benzyl alcohol into benzaldehyde on the CdS and reduction of nitrobenzene into aminobenzene on the TiO_2 surface takes place efficiently. The process for abstraction of α-hydrogen of the benzyl alcohol was found to be the rate-determining step. Moreover, the successive condensation of the photo-produced benzaldehyde and aminobenzene into N-benzylideneaniline was found to take place on the catalyst surface under dark conditions. This work is the first to achieve the one-pot synthesis of imine from benzyl alcohol and nitrobenzene on the visible-light sensitive CdS-TiO_2 photocatalyst without the use of any precious metals as a co-catalyst at 298 K. Both oxidative and reductive products formed in the photocatalytic reaction here participated in the formation of useful products, leading to a new strategy for photocatalysis-based one-pot organic synthesis.

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