저작자표시-비영리-변경금지 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.

다음과 같은 조건을 따라야 합니다:

저작자표시. 귀하는 원저작자를 표시하여야 합니다.

비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.

변경금지. 귀하는 이 저작물을 개작, 변형 또는 가공할 수 없습니다.

- 귀하는 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 이용허락규약(Legal Code)을 이해하기 쉽게 요약한 것입니다.

Disclaimer ▼
Z-Schematic Electron Transfer Dynamics of CdS/Au/C-TiO$_2$ at the Solid-State Interface

CdS/Au/C-TiO$_2$ 광촉매의 고체계면을 통한 Z-Scheme 형태의 전자이동역학 연구

2013년 8월

서울대학교 대학원
화학생물공학부
여정은
Abstract

Z-Schematic Electron Transfer Dynamics of CdS/Au/C-TiO$_2$ at the Solid-State Interface

JUNGEUN YEO

School of Chemical and Biological Engineering
The Graduate School
Seoul National University

In the field of photochemical conversion of the solar light, photocatalytic water splitting have attracted a great deal of interest over the past decades. Among various techniques, semiconductor-based artificial photosynthesis was proposed as an attempt to realize Z-schematic electron utilization of natural photosynthesis. Recently, CdS/Au/C-TiO$_2$ was developed as a visible-light responsive photocatalytic system with Z-schematic electron transfer. In the presence of Au between the two semiconductors, photoinduced electrons in photosystem (PS) II material (C-TiO$_2$) were
transferred to the valence band of PS I (CdS). Although we know that this photocatalytic system can efficiently harvest visible light, the electron transfer mechanism of the system is still unknown. Thus, it is essential to investigate how Au mediates the electron transfer in CdS/Au/C-TiO₂ compared to that in non-mediated system, CdS/C-TiO₂. In this study, CdS/Au/C-TiO₂ and CdS/C-TiO₂ were prepared as the subjects of electron transfer dynamics and investigated with time-resolved photoluminescence (PL) measurement, one of the ultrafast laser techniques monitoring charge carrier dynamics. The temporal PL spectra analysis revealed that the lifetime of C-TiO₂ in CdS/Au/C-TiO₂ system was reduced compared to the bare C-TiO₂, indicating charge transfer from C-TiO₂ to CdS via Au. On the other hand, CdS/C-TiO₂ showed increased lifetime of C-TiO₂ which means electron flow from CdS to C-TiO₂ was occurred. This result supports that the introduction of Au at the heterojunction interface can utilize photoinduced electron transfer in Z-schematic manner achieving enhanced ability to generate H₂ via water splitting upon visible light absorption.

**Keywords:** photocatalysis, Z-scheme, CdS/Au/C-TiO₂, solid-state interface, electron transfer

**Student Number:** 2011-24098
Contents

Chapter 1 Introduction ................................................................. 1

Chapter 2 Experimental.............................................................. 5
  2.1 Preparation of CdS/Au/C-TiO$_2$ ........................................ 5
  2.2 Characterizations ................................................................ 7
  2.3 Photocatalytic activity test ................................................. 8
  2.4 Time-resolved photoluminescence measurement ............... 9

Chapter 3 Results and Discussion ............................................. 10
  3.1 Characterization of CdS/Au/C-TiO$_2$ .................................. 10
  3.2 Photocatalytic activity ........................................................ 15
  3.3 Electron transfer dynamics of CdS/Au/C-TiO$_2$ ................. 17
    3.3.1 Time-resolved photoluminescence spectra .................. 17
    3.3.2 Lifetime analysis ...................................................... 17
    3.3.3 Z-schematic electron transfer of CdS/Au/C-TiO$_2$ .......... 20

Chapter 4 Summary and Conclusions........................................ 28
References..................................................................................................................30

Abstract (in Korean)..................................................................................................33
List of Tables

Table 3-1  Electron transfer paths and rate equations for the radiative paths.24
Table 3-2  Fitting parameters of time-resolved PL spectra..........................25
List of Figures

Fig. 3-1 TEM images of (a) CdS/Au/C-TiO$_2$ and (b) CdS/C-TiO$_2$............10

Fig. 3-2 XRD patterns for C-TiO$_2$, CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$......12

Fig. 3-3 UV-vis absorbance of C-TiO$_2$, CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$ ..........................................................13

Fig. 3-4 H$_2$ evolution via water splitting over CdS/Au/C-TiO$_2$, CdS/C-TiO$_2$ and C-TiO$_2$ ..................................................16

Fig. 3-5 Time-resolved photoluminescence spectra of rhodamine 6G in the presence of C-TiO$_2$, CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$ ........22

Fig. 3-6 Schematic diagram of electron transfer model of CdS/Au/C-TiO$_2$ suspended in rhodamine 6G aqueous solution .............23

Fig. 3-7 Steady-state photoluminescence spectra of rhodamine 6G and C-TiO$_2$ in aqueous solution ..............................................26

Fig. 3-8 Schematic diagram of electron transfer of (a) CdS/Au/C-TiO$_2$ and (b) CdS/C-TiO$_2$ ........................................................27
Chapter 1. Introduction

Solar energy conversion is one of the key technologies in renewable energy society, which can supply alternative energy to fossil fuel and cut the global energy consumption. Climate change caused by greenhouse gases from hydrocarbon fuels has been another major concern, which boosts the demand for sustainable and environmental-friendly energy generation. Among renewable energy sources such as hydroelectricity, tides and ocean currents, geothermal, and wind power, the solar energy strikes the earth with power of tremendous magnitude ($1.2 \times 10^{17}$ watts) far surpassing other resources [1]. Therefore, harvesting incident photons of solar light and converting them into electricity or fuel can give us highly efficient use of solar energy. As an effort, photovoltaic [2] and photoelectrochemical cells [3-5] have been developed over the past decades. Since Fujishima and Honda discovered photocatalytic splitting of water by n-type TiO$_2$ electrode in 1971 [6], semiconductor-based photocatalytic hydrogen evolution via water splitting has been emerged one of the most important technologies to solve the energy challenges. In particular, semiconductor nanostructures have been intensively developed as building blocks to construct photochemical system. However, utilization of solar light by photocatalytic system has a limitation with low efficiency.

Recently, various researches have been studied to develop the efficient photocatalytic system. Many research groups have tried to enhance a
photoconversion efficiency by controlling the size or shape of nanoparticles (nanotube, rod, and wire) [7-9], loading cocatalysts [10-12], using graphene nanocomposites [13-15], and utilizing defect engineering [16]. In particular, the heterojunction of nanostructured semiconductors has attracted a great deal of research interest since coupled semiconductors with suitable band position are convenient to improve charge separation. For instance, CdS/TiO$_2$ nanocomposite is known to be effective for degradation of organic pollutants and photocatalytic water splitting [17, 18]. Upon the absorption of light, vectorial electron transfer occurs from CdS to TiO$_2$ which is responsible for enhanced charge separation by suppressing charge recombination. As an approach to boost charge separation in a more effective manner, three-component systems have been also investigated in recent years [19-21]. Numerous metals and semiconductors have been utilized in various fashions to give composites with appropriate alignment of energy level, which facilitates charge flow to the redox centers. Among the ternary composites, Z-scheme photocatalytic systems of semiconductor-metal-semiconductor have been proposed to realize overall water splitting by mimicking natural photosynthesis [22]. By introducing metal as electron transfer mediator between the heterojunction of two semiconductors, for example in CdS/Au/TiO$_2$ system under UV light irradiation, Au acts as an electron mediator that captures photogenerated electrons from TiO$_2$ and accelerates charge transfer to CdS. As a result, it showed outstanding photocatalytic activity on H$_2$ generation via water splitting, compared to non-mediated system. In addition, Z-scheme operation under visible light
has been demonstrated to fulfill the demand for solar energy utilization [23]. By combining two visible light-responsive photocatalysts, CdS and carbon-doped TiO$_2$ (C-TiO$_2$), the system (CdS/Au/C-TiO$_2$) works under visible light irradiation and shows a highly superior performance in H$_2$ evolution from water, enabling an artificial photosynthesis upon solar energy absorption.

While most of photocatalytic studies focused on the net photoconversion efficiency and have achieved efficient electron utilization, understanding of charge transfer dynamics across the semiconductor interface is still lacking. To design these semiconductor nanostructures for photochemical conversion, kinetics details of interfacial charge transfer should be addressed because this process mainly governs the performance of the system. Toward the demand for monitoring charge dynamics, time-resolved photoluminescence (PL) measurement, one of the ultrafast time-resolved laser techniques [24], has been drawn attentions by providing time profile of fluorescence.

In this study, electron transfer dynamics in Z-schematic CdS/Au/C-TiO$_2$ was examined by time dependent PL measurement for better understanding of charge transfer processes in the system after exciton dissociation. Focusing on the electron dynamics at solid-state interface, we set up the model equations for CdS/Au/C-TiO$_2$ and correlated PL spectra analysis with the equations. Based on the knowledge of photoexcitation and relaxation characteristics of semiconductors, the rate constants of interfacial electron transition were successfully measured. With this model, we could suggest derivation of kinetic parameters from the PL measurement and eventually demonstrate the efficient electron transfer dynamics of CdS/Au/C-TiO$_2$ at
the solid-state interface. In particular, this study can support the role of the Au which was introduced between two semiconductors, C-TiO₂ and CdS, by comparing Au mediated system to binary system (CdS/C-TiO₂) without Au which mediates electron transfer processes.
Chapter 2. Experimental

2.1 Preparation of CdS/Au/C-TiO₂

C-TiO₂ nanoparticles were synthesized by a gel-hydrothermal method. Titanium tetraisopropoxide (60 mL, Samchun) and triethanolamine (54 mL, Sigma) were mixed with 286 mL of deionized water (DI water) to give 400 mL of an aqueous solution, followed by vigorous stirring for 30 min. This solution of 30 mL was mixed with the same amount of oleic acid (0.02 M) aqueous solution and the pH of the mixture was adjusted to pH 8 by adding nitric acid (Samchun, 60%). Gel-type titanium precursor was formed by heating this mixture in Teflon-lined autoclave at 100 °C for 12 h and subsequently heating at 250 °C for 48 h. After washing and drying processes, synthesized C-TiO₂ powder was heated under air atmosphere at 320 °C for 8 h, to remove the organic residue that remains on the surface of C-TiO₂ nanoparticles. Finally, lightly browned C-TiO₂ powder was obtained.

For synthesis of CdS/Au/C-TiO₂ nanoparticles, Au was deposited on C-TiO₂ surface prior to the formation of CdS. As-synthesized C-TiO₂ (0.5 g) was dissolved in aqueous solution (200 mL) of chloroauroic acid which contains 1 wt % of Au over C-TiO₂, and 5 mL of NaBH₄ solution (5.3 M) was gradually added to reduce AuCl₄⁻ into Au. After stirring for 2 h and centrifugation, purple-colored Au/C-TiO₂ can be obtained. For the following formation of Au-CdS core-shell structure, Au/C-TiO₂ (0.45 g) dissolved in
ethanol solution (200 mL) with cadmium perchlorate (8 mmol, Aldrich) and sulfur (2 mmol, Kanto). After sonication for 30 min and vigorous stirring, the mixture was irradiated by UV light for 12 h. Followed by washing and drying of the suspension, we obtained powdered CdS/Au/C-TiO$_2$.

For comparison, CdS/C-TiO$_2$ was synthesized by ion exchange method. As-synthesized C-TiO$_2$ (0.5 g) and sodium sulfide (0.2 mmol, Acros) dissolved in DI water to give 200 mL aqueous solution and then 50 mL of cadmium acetate (0.5 mmol, Sigma) aqueous solution was added in dropwise manner. Washing and drying were followed to produce powdered sample.
2.2 Characterizations

The morphology of materials was examined by high-resolution transmission electron microscopy (HR-TEM, JEM3010, JEOL) operating at 300 kV. A crystalline structure of the samples was verified with X-ray diffraction (XRD, D/max-2500/PC, Rigaku) with Cu Kα radiation (wavelength = 0.154 nm) as the incident beam at 50 kV and 100 mA. The optical absorbance spectra were obtained by ultraviolet diffuse reflectance spectroscopy (UV-DRS, V670, Jasco). Steady-state fluorescence emission spectra were measured by luminescence spectrometer (LS-55, PerkinElmer).
2.3 Photocatalytic activity test

Photocatalytic activity was measured by water splitting test. Prior to the reaction, aqueous suspension (100 mL) of each photocatalyst (0.08 g) was prepared, and Na$_2$S (0.05 M) and Na$_2$SO$_3$ (0.1 M) were added as sacrificial reagents. After vigorous stirring and sonication for 30 min, the solution was put in a Pyrex glass reactor with quartz window and de-aerated with nitrogen gas. A Xe arc lamp (300 W, Oriel) was used as a light source and UV radiation was blocked through long-pass filter ($\lambda > 420$ nm). To prevent temperature rise by the irradiated energy of light, the reactor equipped cooling jacket with circulating coolant of 20 °C. The amount of H$_2$ production was measured by gas chromatography (ACME 6100, YoungLin) with a thermal conductivity detector (TCD).
2.4 Time-resolved photoluminescence measurement

Time-resolved PL was measured by means of time-correlated single photon counting (TCSPC) technique to obtain fluorescence decay and its temporal information. Fluorescence spectrometer (Fluotime 200, PicoQuant GmbH) is equipped with a pulsed diode laser (PDL 800-D), polarizers, monochromator, photon detector (MCP-PMT, R3809U-50 series, Hamamatsu), and temperature-controlled cuvette holder. The sample was excited by a short pulse of light (\(\lambda = 405\) nm) with a repetition rate of 80 MHz whose optical pulse duration is about 64 ps (FWHM).

For lifetime measurement, each photocatalyst suspended in rhodamine 6G (R6G) aqueous solution (1 \(\mu\)M) hold in cuvette at 20 °C was illuminated with excitation light. Laser-induced fluorescence were collected at 550 nm beforehand through a filter (\(\lambda > 435\) nm). The intensity of the photon emission versus time was recorded. The measured PL decay curves were interpreted by fluorescence decay analysis software (FluoFit, PicoQuant GmbH). The curves were fitted by a multi-exponential function described as

\[
I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i}
\]

where \(A_i\) is amplitude in counts and \(\tau_i\) is lifetime of the \(i^{th}\) component. For performing a fitting procedure with best agreement between experimental data and theoretical model, adjustive fitting procedure was repeated with minimized error which is addressed by reduced chi-squared value (\(\chi^2\)).
Chapter 3. Results and discussion

3.1 Characterization of CdS/Au/C-TiO$_2$

As a photocatalytic system of interest in this study, CdS/Au/C-TiO$_2$ was prepared to investigate the efficient charge utilization at the solid-state interface compared to CdS/C-TiO$_2$. First, C-TiO$_2$ nanoparticles were synthesized by dissolution-recrystallization of gel-type titanium precursor in the presence of oleic acid as previously reported [23]. Carboxyl group of oleic acid was adsorbed to the TiO$_2$ seed materials, providing carbon dopants into TiO$_2$ framework. Au was deposited on the surface of C-TiO$_2$ by direct reduction of AuCl$_4^-$ ion with NaBH$_4$. In sequence, CdS was synthesized when Au/C-TiO$_2$ was dispersed in ethanol solution with sulfur and cadmium ion. Irradiated by UV light, sulfur was reduced to S$^{2-}$ ion at the surface of Au because sulfur has a great affinity to Au atoms [25]. Then, S$^{2-}$ ion reacts with Cd$^{2+}$ ion, coating Au nanoparticle with CdS layer. The TEM images of CdS/Au/C-TiO$_2$ nanoparticles showed that CdS were synthesized selectively onto Au nanoparticles forming hemispherical core-shell structures on the surface of C-TiO$_2$ (Figure 3-1a). The diameter of Au cores is about 4 to 10 nm and those were covered with CdS whose thickness is in the range from 4 to 7 nm. The lattice arrays of CdS in Figure 3-1a (inset) showed interplanar spacing ($d = 3.75$ Å) which corresponds to [100] plane of wurtzite CdS, indicating successful development of CdS.

CdS/C-TiO$_2$ nanoparticles were synthesized for the comparison with
CdS/Au/C-TiO$_2$ to demonstrate the effect of Au lying between the two semiconductors. The morphology of CdS/C-TiO$_2$ was displayed in Figure 3-1b. Agglomerated CdS on the C-TiO$_2$ surface had the diameter in the range of 5 to 15 nm without defined shape, showing interplanar distance identical to the wurtzite crystalline of CdS. The structure of CdS was also established by X-ray diffraction patterns shown in Figure 3-2. The weak signals of wurtzite crystalline CdS were found in both CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$. In addition, all samples based C-TiO$_2$ were verified to have anatase polycrystalline without any other phases.

UV-visible diffused reflectance spectra shown in Figure 3-3 enables the estimate of the band gap energy ($E_g$) of semiconductors employed. Linear extrapolation of the shoulder observed in C-TiO$_2$ indicates that C-TiO$_2$ has $E_g$ of 2.6 eV. CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$ showed another absorption shoulder in the range of 400 – 500 nm, which is originated from CdS.

Although $E_g$ of CdS was reported as 2.3 eV [23], the extrapolation of the shoulder appointed around 610 nm, longer wavelength than expected, indicating the blueshift of the absorption edge of CdS in composite system. This shift is in agreement with the previous research that CdS band gap is shifted by an electronic semiconductor-support interaction [26], indicating that CdS has heterojunction interface with C-TiO$_2$. Additional absorption peak around 630 nm of CdS/Au/C-TiO$_2$ was attributed to surface plasmon of Au nanoparticle [27]. The findings represent that CdS/Au/C-TiO$_2$ nanoparticles were successfully prepared.
Figure 3-1. TEM images of (a) CdS/Au/C-TiO$_2$ and (b) CdS/C-TiO$_2$. Hemispherical core-shell structures of Au/CdS were found on the surface of C-TiO$_2$ in case of CdS/Au/C-TiO$_2$. The interplanar spacing (d = 3.57 Å) of CdS indicates [100] plane of wurtzite CdS
**Figure 3-2.** The XRD patterns for C-TiO$_2$, CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$ nanoparticles. Crystalline C-TiO$_2$ was verified as anatase structure and weak signal of wurtzite CdS was found in both CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$. 

- **Wurtzite**
- **Anatase**

![XRD Patterns](image)

\[2\theta \ (^\circ)\]

- CdS/C-TiO$_2$
- CdS/Au/C-TiO$_2$
- C-TiO$_2$
Figure 3-3. UV-vis absorbance of C-TiO$_2$, CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$. The energy band gap of C-TiO$_2$ was determined as 2.6 eV by linear extrapolation of the first shoulder. CdS/C-TiO$_2$ has another shoulder in the range of 400-500 nm which is slightly blue-shifted from the absorption edge of CdS (E$_g$ = 2.3 eV). Absorption peak around 630 nm is attributed to the surface plasmon of Au nanoparticles.
3.2 Photocatalytic activity

The photocatalytic activity of prepared samples was evaluated by the ability to generate H$_2$ via splitting of water. The amount of H$_2$ production over CdS/Au/C-TiO$_2$, CdS/C-TiO$_2$ and C-TiO$_2$ were presented in Figure 3-4. Under visible light irradiation (λ > 420 nm), CdS/Au/C-TiO$_2$ showed the highest H$_2$ evolution rate (7.5 μmol/h), surpassing CdS/C-TiO$_2$ (1.1 μmol/h) by about 7 times. This result means that larger amount of electrons were participated in the redox reaction with water, reducing adsorbed H$_2$O molecules into H$_2$. The enhanced photocatalytic performance of CdS/Au/C-TiO$_2$ provided the need to study dynamics on the system to answer the question that how the system was changed by introducing Au nanoparticles.
Figure 3-4. H₂ evolution via water splitting over CdS/Au/C-TiO₂, CdS/C-TiO₂ and C-TiO₂. H₂ evolution rate of CdS/Au/C-TiO₂ is about 7 times higher than CdS/C-TiO₂.
3.3 Electron transfer dynamics of CdS/Au/C-TiO$_2$

3.3.1 Time-resolved photoluminescence spectra

Time-resolved PL measurement was done to elucidate an electron utilization of the photocatalytic system, in particular CdS/Au/C-TiO$_2$. For the PL detection, R6G was used as an indicator dye with the intention of reducing scattering effect and facilitating monitoring of electron-enriched system. We employed 405 nm pulsed laser for band gap excitation of both C-TiO$_2$ and CdS. The PL emission spectra of C-TiO$_2$, CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$ in R6G aqueous solution were displayed in Figure 3-5. Compared to the R6G solution, the spectra showed reduced maximum count, indicating occurrence of fluorescence quenching. In general, the fluorescence largely made by dye molecules are quenched via electron transfer processes if there are quenching agents, inferring that excited electrons in R6G transferred to the semiconductor nanoparticles. Having acquired PL decay curves, the kinetic information was extracted by fitting the fluorescence decay. Based on the exponential nature of fluorescence decay, the curves were represented by a multi-exponential function.

3.3.2 Lifetime analysis

For PL spectra analysis, we addressed a hypothetic kinetic model for CdS/Au/C-TiO$_2$ suspended in R6G aqueous solution. Figure 3-6 illustrates the schematic diagram of electron transfer processes. Based on the
photophysical properties of the system, the scheme described states of electrons and intrinsic and interfacial charge transfer processes. For each transfer pathway, the rate constant ($k$) are numbered sequentially from left to right. Excited and ground states of a semiconductor were denoted as $N^*$ and $N$ respectively, with subscript R, T, and C indicating R6G, C-TiO$_2$ and CdS. Contrast to semiconductors, Au was regarded as an electron mediator where photoinduced electron transportation occurred from photosystem (PS) II (C-TiO$_2$) to PS I (CdS). According to the electron flow, both intrinsic and interfacial electron transfer paths were arranged as shown in Table 3-1. Each case (Case 1 – 4) was classified by the materials involved. Based on the possible paths, rate equations were derived and also summarized in Table 3-1. Here electron transfer reaction was assumed to follow first-order kinetics [28]. For $N_R$, the equation was expressed as monoexponential function, whereas $N_T$ decayed in bi-exponential fashion. Based on the theoretical equations, the intensity of PL spectra were analyzed by exponential function described as

$$I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i}$$

For the time-resolved spectra of R6G, the lifetime of R6G was obtained by fitting the curve in a mono-exponential fashion. Table 3-2 shows the fitting results of the PL decay curves. In Case 1, fitting parameters yield the lifetime of R6G ($\tau_1 = 3.93$ ns) close to the reported value [29]. Then, the rate constant $k_1$ was computed by the simple expression $k_1 = 1/\tau_1$ given by $\tau_1$ ($k_1 = 2.54 \times 10^8$ s$^{-1}$).
Upon the addition of C-TiO\textsubscript{2} nanoparticles in R6G solution (Case 2), the PL curve was finely fitted by bi-exponential functions and two lifetimes, $\tau_1$ and $\tau_2$ were obtained. The shorter lifetime ($\tau_1 = 3.83$ ns) is related to the electron population decay of R6G, and the small extent of reduced lifetime is originated from the charge injection into the CB of C-TiO\textsubscript{2}. Driven by the potential difference between the lowest unoccupied molecular orbital (LUMO) level of R6G (~ -1.0 V vs NHE) [30] and C-TiO\textsubscript{2} CB edge (-0.5 V vs NHE) [31], excited population $N_{R*}$ has two way of transfer. As the result, $k_1$ was replaced with $k_1 + k_2$ in equation 2a and $k_2$ (6.64 x 10\textsuperscript{6} s\textsuperscript{-1}) was determined from the shortened lifetime of R6G by the modified relation; $1/\tau_1 = k_1 + k_2$. On the other hand, additional longer lifetime ($\tau_2 = 9.82$ ns) was regarded as being originated from C-TiO\textsubscript{2}, representing the lifetime of electrons populated in C-TiO\textsubscript{2}. Since the fluorescence emission of both R6G and C-TiO\textsubscript{2} contribute to the emission spectra at 550 nm, correlation of second exponential term in equation 2b with $\tau_2$ are feasible ($k_3 = 1.02 \times 10^8$ s\textsuperscript{-1}). Overlapping PL emission of C-TiO\textsubscript{2} and R6G at 550nm was supported by steady-state fluorescence spectra shown in Figure 3-7, even though the contribution of C-TiO\textsubscript{2} is much less than that of fluorescent R6G.

Given by $k_1$, $k_2$, and $k_3$, the interfacial electron transfer rate was delivered by $k_4$. As the scheme represented, conduction band electrons of C-TiO\textsubscript{2} moved in two ways; mostly due to the recombination with hole driven by Coulombic attraction, and alternatively to the charge transportation across the solid state interface. In comparison of Case 2, the rate equation of $[N_{R}]$ remains unchanged in equation 3a and $k_3$ was substituted by $k_3 + k_4$ in
equation 3b. While \( \tau_1 \) was fixed, \( \tau_2 \) was determined by fitting tool, exhibiting reduced lifetime of C-TiO\(_2\) (9.82 → 6.61 ns). Finally, \( k_4 \) \( (4.95 \times 10^7 \text{ s}^{-1}) \) was calculated, which is descriptive of the electron transfer rate from C-TiO\(_2\) to the CdS via Au nanoparticles. Compared to the recombination process, the rate constant of charge transfer reaction through the solid-state interface is smaller by an order. In the absence of Au (Case 4), the rate constant for electron transfer between C-TiO\(_2\) and CdS (call \( k_4' \) instead of \( k_4 \)) was determined in the same manner \( (k_4' = -6.87 \times 10^6 \text{ s}^{-1}) \).

3.3.3 Z-schematic electron transfer of CdS/Au/C-TiO\(_2\)

Compared to \( k_4 \), \( k_4' \) showed negative value, indicating that the majority of electrons transferred from CdS (CB) to C-TiO\(_2\) (CB) when C-TiO\(_2\) is coupled with CdS. Similarly, the vectorial charge transfer between two coupled semiconductors was known from CdS/TiO\(_2\) nanojunction photoexcited system [18]. Otherwise, we regard photogenerated electrons of C-TiO\(_2\) (CB) in CdS/Au/C-TiO\(_2\) system flow into Au with large work function (5.1 eV) [22] until the Fermi level aligns at equilibrium, and gradually flowed the lower energy level of CdS to combine with holes left in CdS (VB). Finally electron populations in excited state of CdS can participate in redox reaction with absorbed substrate at the surface, exhibiting simultaneous electron transfer in form of Z-scheme. Although electrons are allowed to flow from CdS to C-TiO\(_2\) in the system, \( k_4 \) value derived from this experiment indicates that back electron transfer from CdS
to C-TiO$_2$ is a minor path, strongly supporting the vectorial electron transfer in Z-schematic system (Figure 3-8). Even though this does not entirely explain the superiority of the system, we reveal that Au mediated the electron transfer toward CdS, allowing the reduction occur at CdS surface. Compare to the C-TiO$_2$, higher CB level (-1.0 V vs NHE) [17] of CdS is advantageous to reduce water to hydrogen driven by larger potential difference, which is attributed to the superior performance toward water splitting.
Figure 3-5. Time-resolved PL spectra of suspensions recorded at 550 nm.
Figure 3-6. The schematic diagram of electron transfer model of CdS/Au/C-TiO$_2$ suspended in R6G aqueous solution. N* indicate excited states while N stands for bound states of an electron. Subscript R, T and C indicate R6G, C-TiO$_2$ and CdS respectively. Kinetic constants, $k$, are numbered sequentially from R6G to CdS. $k_1$ : relaxation rate constant in R6G, $k_2$ : electron transfer rate constant from R6G to C-TiO$_2$ (CB), $k_3$ : recombination rate constant of C-TiO$_2$, and $k_4$ : electron transfer rate constant from C-TiO$_2$ (CB) to CdS (VB) via Au core
In Case 4, R6G and CdS/C-TiO₂ are a subject of the interest and \( k₄' \) replaces of \( k₄ \).

* \( C₁ = \frac{k₃k₂}{k₃(k₁+k₂)} \) and \( C₂ = \frac{k₃k₂}{(k₃+k₂)(k₁+k₂)} \)

Table 3-1. Electron transfer paths and rate equations for the radiative paths
<table>
<thead>
<tr>
<th>Materials</th>
<th>$A_1$</th>
<th>$\tau_1$</th>
<th>$A_2$</th>
<th>$\tau_2$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Case 1) R6G</td>
<td>32280</td>
<td>3.93</td>
<td>-</td>
<td>-</td>
<td>1.078</td>
</tr>
<tr>
<td>(Case 2) R6G, C-TiO$_2$</td>
<td>16835</td>
<td>3.83</td>
<td>393</td>
<td>9.82</td>
<td>1.024</td>
</tr>
<tr>
<td>(Case 3) R6G, CdS/Au/C-TiO$_2$</td>
<td>23066</td>
<td>3.83</td>
<td>438</td>
<td>6.61</td>
<td>1.018</td>
</tr>
<tr>
<td>(Case 4) R6G, CdS/C-TiO$_2$</td>
<td>23093</td>
<td>3.83</td>
<td>113</td>
<td>10.53</td>
<td>1.067</td>
</tr>
</tbody>
</table>

*Table 3-2. Fitting parameters of time-resolved PL spectra.*
**Figure 3-7.** Steady-state PL spectra of R6G and C-TiO$_2$ in aqueous solution. The wavelength of excitation source was 405 nm and long-pass filter (495 nm) was used.
Figure 3-8. Schematic diagram of (a) CdS/Au/C-TiO$_2$, and (b) CdS/C-TiO$_2$. 
Chapter 4. Summary and Conclusions

In this study, we demonstrated that the Z-schematic electron transfer dynamics was realized at the solid-state interface of CdS and C-TiO$_2$ system, by introducing Au as an electron mediator. Au and CdS were deposited on the surface C-TiO$_2$ nanoparticles to form Au/CdS hemispherical core-shell structure. Water splitting test showed that H$_2$ evolution rate of CdS/Au/C-TiO$_2$ was 7 times higher than CdS/C-TiO$_2$. To investigate the electron transfer mechanism derived by Au, the lifetime of two photocatalysts, CdS/Au/C-TiO$_2$ and CdS/C-TiO$_2$, was measured by time-resolved PL spectroscopy. To analyze the PL time decay, a hypothetic kinetic model for CdS/Au/C-TiO$_2$ was introduced. The rate constants obtained from the fitting parameters indicated that Au/CdS core-shell on the surface of C-TiO$_2$ reduced the lifetime of C-TiO$_2$, indicating the occurrence of interfacial charge transportation from C-TiO$_2$ to adjacent materials. In case of non-mediated system (CdS/C-TiO$_2$), the lifetime was increased due to the charge injection from CdS to C-TiO$_2$. This reveals that Au played an essential part in altering the passage of charge carriers, allowing vectorial electron transfer from C-TiO$_2$ to CdS, demonstrating Z-schematic electron operation. As a result, photoinduced electrons in the excited-state of CdS have higher potential energy for water reduction, which underlies the superior performance of CdS/Au/C-TiO$_2$ system toward photocatalytic water splitting. This experimental approach opens a new window to identify the possible transfer channel and to
investigate the role of electron mediator when two semiconductors of different energy level are coupled to form solid-state heterojunction interface.
References


[31] D. Kuciauskas, M. S. Freund, H. B. Gray, J. R. Winkler, N. S. Lewis, *J.
태양에너지 전환 기술이 화석연료를 대신할 수 있는 친환경·지속 가능한 에너지원으로 각광받고 있는 가운데, 광촉매를 이용하여 물로부터 수소를 발생시키는 기술이 큰 관심 속에서 연구되고 있다. 그 중 녹색식물이 태양빛을 이용하여 물로부터 에너지를 얻는 광합성작용을 모방하여, 인공적으로 광합성을 구현하는 광촉매 물질에 대한 연구가 이루어졌다. 최근 가시광을 흡수할 수 있는 화화카드뮴 (CdS)과 탄소가 도핑된 이산화티탄 (C-TiO$_2$)을 자연광합성에서의 광계 I, 광계 II 물질로 사용하고, 금 (Au)을 전자매개체로 사용하여 가시광 영역의 에너지를 흡수하여 물분해 수소생산이 가능한 광촉매 시스템 (CdS/Au/C-TiO$_2$)이 발표되었다. 이 물질에서는 C-TiO$_2$가 빛을 흡수하여 전도대에 전자를 발생시키고, 이 전자가 Au를 통해 CdS로 이동하여 가전자대에 있는 전공과 결합한다. 동시에 CdS도 빛을 흡수하여 전도대로 전자를 발생시키고, 결국 Z 모양을 이루어 전자가 이동하게 된다고 알려져 있다. 따라서 이 연구에서는 CdS/Au/C-TiO$_2$ 광촉매에서의 전자이동을 CdS/C-TiO$_2$와 비교하여, 금을 전자 매개체로 하였을 때 전자이동의 에너지층이 Z 형태로 달라지는 것을 확인하고자 한다. 이를 위해 CdS/Au/C-

주요어: Z-스킴, 광촉매, CdS/Au/C-TiO$_2$, 고체계면, 전자이동

학 번: 2011-24098