Kinetic and Mechanistic Insights into the All-Solid-State Z-Schematic System

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Supporting Information

ABSTRACT: An all-solid-state Z-schematic system, CdS/Au/TiO1.96C0.04, has been reported for the efficient H2 generation from water under visible-light irradiation. However, a kinetic and mechanistic study of the directionional charge transfer at the interfaces has not been done. In this study, electron pathways were constructed on the basis of steady-state photoluminescence (PL) spectral data, and the rate constants for charge transfer were calculated from time-resolved PL spectra. The PL results revealed that Au core played an important role in capturing the photoexcited electrons in the conduction band (CB) of TiO1.96C0.04 and accelerating the electron transfer to the valence band (VB) of CdS, leading to an efficient quenching of the holes left in the VB of CdS shell. The minimum energy pathways for H2 production on the surfaces of TiO1.96C0.04(101) and CdS(101) were elucidated through first-principles calculations, indicating that the CdS shell has a lower energy barrier (2.81 eV) for the surface reaction than that (3.34 eV) of TiO1.96C0.04. Consequently, CdS/Au/TiO1.96C0.04 showed a vectorial electron transfer of TiO1.96C0.04 → Au → CdS in the form of the letter Z, which allowed the photoexcited electrons to be shuttled to a higher energy level, thereby producing a substantial level of H2 on the CdS(101) surface.

1. INTRODUCTION

Hydrogen, H2, is a potential alternative to fossil fuels for achieving a sustainable society. Approximately 95% of emission-free H2 has been produced by steam-methane reforming process which involves the side production of carbon dioxide and carbon monoxide, ironically contributing to global warming.1 One of the most promising technologies for environmentally producing carbon-free H2 is artificial photosynthesis mimicking the natural process of photosynthesis as follows.2–6 The electrons in the VB of photosystem (PS) II are excited to its CB under irradiation by solar light. The photoexcited electrons are transferred to the VB of PS I through an electron mediator where the transferred electrons recombine with the holes left in the VB of PS I. The photoexcited electrons and holes accumulate in the CB of PS I and the VB of PS II, respectively. Consequently, they have thermodynamically strong redox characteristics to allow solar light to be efficiently converted into chemical energy. This charge-transfer mechanism is the so-called Z-scheme.

We recently reported that two visible-light responsive photocatalysts, TiO1.96C0.04 and CdS, when combined with Au nanoparticles, generate H2 from water via the artificial Z-scheme mechanism.6 The photocatalytic system utilized the CdS and TiO1.96C0.04 as the components of PS I and PS II in green plants, respectively. Au nanoparticles acted as an electron mediator between TiO1.96C0.04 and CdS. The CdS/Au/TiO1.96C0.04 system achieved the efficient H2 production when irradiated with visible light. However, the vectorial charge-carrier flow at the interface was not fully investigated from the standpoint of kinetics and mechanism. It is noteworthy that only a few kinetic and mechanistic studies have been conducted with the goal of comprehending the complex charge-transfer processes in semiconductor—metal—semiconductor systems.7 In particular, since the issue of charge transfer across the semiconductor interface is a key factor in enhancing photocatalytic activity, kinetic and mechanistic insights into an all-solid-state Z-schematic system are essential and important for a fundamental understanding of such a system and the practical applications of artificial photosynthesis.

In this study, the Z-schematic charge-transfer kinetics of CdS/Au/TiO1.96C0.04 was demonstrated by measuring the decay time of an indicator dye through steady-state PL and time-resolved PL spectroscopy, one of the ultrafast laser techniques that are used to probe interfacial charge transfer in photocatalysis.8–12 Electron pathways were constructed on the basis of the results of steady-state PL spectroscopy, so as to understand kinetics of the charge-transfer processes. Differential equations were derived for use as an effective tool for modeling and understanding the target system. Finally, the rate constants for interfacial charge transfer were calculated by correlating the transport model equation with the kinetic parameters extracted from time-resolved PL spectra. Furthermore, the minimum-energy pathways for associative desorption of H2 on the surfaces of TiO1.96C0.04(101) and CdS(101) were elucidated through the climbing image-nudged elastic band (CI-NEB) method.

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2. EXPERIMENTAL SECTION

2.1. Sample Preparation. TiO1.96C0.04 nanoparticles were prepared by a gel-hydrothermal method. A 60 mL aliquot of titanium isopropoxide (≥99%, Samchun) was completely mixed with 54 mL of anhydrous triethanolamine (≥98%, Sigma-Aldrich), and 286 mL of deionized water (DI water) was then added to the mixture. A 30 mL aliquot of aqueous solution of oleic acid (0.02 M, Samchun) was then mixed with the 30 mL of the prepared solution. The pH of the resulting solution was controlled to pH 8 by the dropwise addition of dilute nitric acid (≥60%, Samchun). The resulting mixture was placed in a Teflon-lined autoclave and heated at 100 °C for 12 h to form a Ti(OH)4 gel, which was then heated at 250 °C for 48 h. The resulting brown precipitate was isolated by centrifugation, washed several times with DI water, and then dried at 60 °C overnight. The organic residue remaining on the surface of the TiO1.96C0.04 nanoparticles was completely removed by annealing at 320 °C for 8 h under an atmosphere of air. Anatase TiO2 nanoparticles were prepared by the procedure described above, except that a calcination temperature of 450 °C was used. Au nanoparticles were deposited on the surface of the TiO1.96C0.04 by direct reduction. TiO1.96C0.04 powder (1.0 g) was dispersed in 200 mL of DI water. HAuCl4·4H2O (≥99.9%, Sigma-Aldrich) was then added to the suspension, resulting in the deposition of 2 wt % Au nanoparticles. After stirring for 30 min, 30 mL of an aqueous solution of NaBH4 (0.02 M) was slowly added to the aqueous suspension. A purple Au/TiO1.96C0.04 powder was obtained after stirring for 3 h and isolated by centrifugation. An Au-CdS core-shell was formed by the photoexcitation of the TiO1.96C0.04. Sulfur (2 mmol) and Cd(ClO4)2·6H2O (8 mmol) were added to 200 mL of an ethanol suspension containing Au/TiO1.96C0.04 nanoparticles. The suspension was exposed to UV light for 12 h using a Xe arc lamp (300 W, Oriel) as the light source. Finally, a dark green CdS/Au/TiO1.96C0.04 powder was obtained by centrifugation, which was washed several times with DI water and dried at 60 °C overnight. The Cs2 content was determined to be 4 wt % by ICP-AES. A heterojunction CdS/TiO1.96C0.04 was prepared by an ion-exchange method. Cd(ClO4)2·6H2O was added to a TiO1.96C0.04 suspension, resulting in the deposition of 4 wt % CdS. After stirring for 30 min, 20 mL of an aqueous solution of Na2S (0.02 M) was slowly added to the suspension. A yellow CdS/TiO1.96C0.04 powder was obtained after stirring for 3 h, which was isolated by centrifugation.

2.2. Catalyst Characterization. The morphology and 2D elemental mapping of the product were investigated by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEM-2100F, 200 kV) equipped with the energy dispersive spectroscopy (EDS). The microstructures were examined by X-ray diffraction (XRD, D/max-2500/PC, Rigaku) with Cu Kα radiation (λ = 0.154 nm) as the incident beam at 50 kV and 100 mA. Optical absorbance spectra were obtained by ultraviolet-visible diffuse reflectance spectroscopy (UV-DRS, V670-Jasco) with BaSO4 as a reference. O 1s spectra of bare TiO2 and TiO1.96C0.04 nanoparticles were obtained by X-ray photoelectron spectroscopy (XPS, Thermo) where the binding energy was corrected with reference to the C 1s peak of 284.5 eV for each sample. The amount of Au or CdS in the prepared samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICPS-7500, Shimadzu).

2.3. Photoluminescence Spectroscopies. The steady-state PL was measured with a PerkinElmer LSS5 spectrophotometer (PerkinElmer Ltd., Beaconsfield, UK) equipped with a Xe lamp. The measurements were replicated a total of three times, and average values were reported. Time-resolved PL spectra were obtained using a time-correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH) with a PicoHarp 300. The excitation source was a 405 nm pulsed diode laser (LDH-P-C-405, Picoquant GmbH) with a repetition rate up to 80 MHz. The signals were collected at the excitonic emission of rhodamine B (RhB, Sigma, for fluorescence, λem = 580 nm). The temperature was maintained at 20 °C by circulating water through an external temperature-controlled device during the TRPL measurements. The measured data from the PicoHarp 300 were analyzed by the FluorFit software.

2.4. Computational Details. Density functional theory (DFT) calculations were carried out with the Vienna ab initio simulation package (VASP), using the generalized gradient approximation Perdew–Burke–Ernzerhof (GGA-PBE) exchange-correlation functional. The projector augmented wave (PAW) method as implemented in the VASP was employed. A plane-wave cutoff energy of 400 eV was used for the calculations including CdS and TiO1.96C0.04. A 3 × 3 × 1 Monkhorst–Pack k-point mesh was used to sample the Brillouin zone. All the structural optimizations were performed until the atomic forces were less than 0.03 eV Å−1. The electronic self-consistent field tolerance was set to 1 × 10−4 eV. Based on the anatase TiO2 (Ih/moncl, JCPDS 21-1272) with 24 Ti atoms and 48 O atoms in a 10.45 × 7.72 × 20.00 Å3 supercell, the TiO1.96C0.04(101) slab was modeled at which one O atom on the surface was substituted with C atom according to the experimental results that lattice oxygen of anatase TiO2 was successfully replaced by carbon dopant (Figure S1a). The CdS slab was constructed by cutting the bulk greenockite structure (P63mc, JCPDS 41-1049) for (101) surface to be exposed, based on the experimental crystallographic results in this study. The constructed slab contained total 54 atoms, which consists of 27 atoms for each Cd and S in a 11.83 × 12.41 × 18.08 Å3 supercell (Figure S1b). The angle between two basal plane vectors which are perpendicular to z-axis is about 105°. The surface of each slab was allowed to be relaxed, and the supercells included the vacuum layer which is thick enough to prevent the slab–slab interactions. The CI-NEB method was used to find the minimum-energy paths for associative desorption of hydrogen. Structural optimizations of initial and final states were performed after systematically screening the possible adsorption states. To set a series of images for the NEB calculation, three images were introduced by linear interpolation of initial and final states with a few modifications to prevent improbable paths. In the following step, partial optimization was performed at the edge of energy barrier to see if another energy barrier emerges. In the NEB calculations, the optimization continued until the maximum atomic forces became less than 0.06 eV Å−1.

2.5. Photocatalytic Activities. Photocatalytic H2 production was performed in a gas-closed top window (quartz glass) Pyrex cell with 0.15 g of photocatalyst suspended in 100 mL aqueous solution of 0.05 M Na2S and 0.1 M Na2SO3. The reaction cell was irradiated with a 300 W Xe lamp (Oriel) combined with a 420 nm cutoff filter. The reaction temperature was maintained by circulating a coolant connected to a water-jacketed reservoir at 15 °C. The amount of produced H2 was
quantified by online gas chromatography (Acme6100-Young Lin) using a thermal conductivity detector (TCD).

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. In the previous research, we reported on the preparation of a visible-light-responsive photocatalyst to mimic the natural photosynthesis. The photocatalytic system was composed of three components: Au-CdS core–shell on the TiO$_{1.96}$C$_{0.04}$-4. Briefly, the TiO$_{1.96}$C$_{0.04}$ nanoparticles synthesized by a gel-hydrothermal method in the presence of oleic acid as a carbon source. Au nanoparticles were deposited on the surface of the TiO$_{1.96}$C$_{0.04}$ by the direct reduction of AuCl$_4^-$ anions to Au$^0$ using NaBH$_4$ as the reducing agent. A CdS shell was selectively formed around the Au core by the photodeposition of an ethanol suspension containing Au/TiO$_{1.96}$C$_{0.04}$ sulfur molecules, and Cd$^{2+}$ cations. Figure 1a shows a HAADF-STEM image of the as-prepared nanocomposite using microscopy techniques. (a) HAADF-STEM image of the Au-CdS core–shell distributed on the surface of TiO$_{1.96}$C$_{0.04}$ nanoparticle at which inset shows the area selected for the STEM-EDS analysis. (b–d) 2D atomic mapping of the core–shell structure selected in the inset of (a); Au, Cd, and S. (e) HR-TEM image showing the lattice fringes of the TiO$_{1.96}$C$_{0.04}(101)$ and CdS(101) planes.

Cds/Au/TiO$_{1.96}$C$_{0.04}$ nanoparticles, in which the thickness of the CdS shells was in the range of 4–5 nm around the Au cores with diameter of 4–6 nm. Figure 1b–d display the results of 2D atomic mapping obtained for a selected area in the inset of Figure 1a, which confirms that a Au-CdS core–shell was successfully formed on the surface of TiO$_{1.96}$C$_{0.04}$. The HR-TEM image shown in Figure 1e clearly reveals two distinct types of lattice fringes, which are assigned to TiO$_{1.96}$C$_{0.04}$ and CdS(101).

The fact that carbon was substitutionally incorporated by replacing lattice oxygen in the TiO$_2$ framework was determined by XRD, TPO, XANES, and EXAFS in the previous study. Furthermore, Figure 2a shows that the carbon dopant has a direct influence on the binding energy (BE) of the O 1s of TiO$_2$. Peak 1 centered at 529.7 eV is assigned to regular lattice oxygen and the BE was maintained, even after carbon doping. Peaks 2 and 3 correspond to carbonate in the TiO$_2$, which is from carbon contamination and adsorbed molecular H$_2$O as the sample is exposed to air. The two peaks were slightly shifted to lower BE due to the formation of oxygen vacancies. The BE shift also verified that the carbon dopants were successfully incorporated into the TiO$_2$ framework. The crystalline structure of the prepared samples was confirmed from XRD patterns (Figure 2b). TiO$_{1.96}$C$_{0.04}$ nanoparticles had an anatase structure in the absence of any other crystalline phase created by the carbon dopants. A typical diffraction peak corresponding to Au nanoparticles was not observed due to its low concentration (2 wt %) as well as the relatively strong diffraction intensity of the anatase structure. Wurtzite diffraction peaks (dotted lines) of 4 wt % CdS were weakly observed in XRD patterns of CdS/Au/TiO$_{1.96}$C$_{0.04}$. Notably, the strongest characteristic peaks of TiO$_{1.96}$C$_{0.04}$ and CdS represented that they mainly exposed (101) surfaces on the each nanoparticles. The absorbance of each sample was characterized by UV-DRS (Figure 2c). One shoulder in area 1 was attributed to TiO$_{1.96}$C$_{0.04}$ and the other shoulder in area 2 corresponded to the presence of CdS shells. In particular, CdS/Au/TiO$_{1.96}$C$_{0.04}$ nanostructure produced a broad peak centered at 600 nm due to the surface plasmon of the Au cores. The plasmon band showed a broadening and red-shift of 55 nm as compared to Au/TiO$_{1.96}$C$_{0.04}$, suggesting that the Au core and the CdS shell are involved in strong electronic interactions. Photocatalytic H$_2$ production was performed at a wavelength longer than 420 nm (Figure 2d). The photocatalytic activity of CdS/Au/TiO$_{1.96}$C$_{0.04}$ was compared with that of bare TiO$_{1.96}$C$_{0.04}$ and CdS-sensitized TiO$_{1.96}$C$_{0.04}$ (CdS/TiO$_{1.96}$C$_{0.04}$) in which all of the samples contained almost the same concentrations of Au and CdS, as determined by ICP-AES. As the particle size and interfacial properties of CdS play a critical role in the photocatalytic activity, the CdS/TiO$_{1.96}$C$_{0.04}$ heterostructure was carefully prepared by slowly adding the dilute Na$_2$S solution into the aqueous suspension of TiO$_{1.96}$C$_{0.04}$ and CdS cations for high dispersion of CdS nanoparticles. Figure 2e shows the morphology and size of CdS nanoparticles dispersed on the TiO$_{1.96}$C$_{0.04}$. Although the CdS nanoparticles were slightly aggregated on a portion of TiO$_{1.96}$C$_{0.04}$ surface, they have a uniform size of 5–8 nm and spherical shape. The bare TiO$_{1.96}$C$_{0.04}$ nanoparticles generated negligible amounts of H$_2$ gas due to the rapid charge recombination of the single photocatalyst and relatively low CB minimum (−0.1 V vs NHE). The CdS/TiO$_{1.96}$C$_{0.04}$ photocatalyst produced 1.2 μmol h$^{-1}$ of H$_2$, and the H$_2$ production resulted from the enhanced charge separation with the formation of a heterojunction structure. The charge separation in the heterojunction structures has been studied by various researchers. Since both the CB minimum (−1.0 V vs NHE) and VB maximum (+1.3 V vs NHE) of CdS are located at more negative potentials than the CB minimum (−0.1 V vs NHE) and VB maximum (+2.5 V vs NHE) of TiO$_{1.96}$C$_{0.04}$, the photoexcited electrons in the CB of the CdS can transfer to the CB of the TiO$_{1.96}$C$_{0.04}$ whereas the photoexcited holes in the VB of TiO$_{1.96}$C$_{0.04}$ can migrate to the VB of CdS. Interestingly, the CdS/Au/TiO$_{1.96}$C$_{0.04}$ photocatalyst produced 6 times more H$_2$ (7.5 μmol h$^{-1}$) than the CdS/TiO$_{1.96}$C$_{0.04}$. This is the result of vectorial charge transfer induced by the simultaneous excitation of TiO$_{1.96}$C$_{0.04}$ and CdS with the participation of Au as an electron mediator. Furthermore, the charge carriers of CdS/Au/TiO$_{1.96}$C$_{0.04}$ nanostructure flow in the reverse direction of the charge transfer in the case of CdS/TiO$_{1.96}$C$_{0.04}$ heterojunction structure. That is, the photoexcited electrons and holes tend to accumulate in the CB of CdS and the VB of TiO$_{1.96}$C$_{0.04}$, respectively. It is thermodynamically plausible that H$_2$ is produced more easily on the surface of CdS via the Z-schematic
electron-transfer pathway compared to the electron-transfer pathway of heterojunction. However, the kinetic and mechanistic aspects of such a junction type are not fully understood.

3.2. Surface-Reaction Energetics. We carried out DFT calculations to find minimum energy pathways for associative desorption of H\textsubscript{2} using the NEB method. First, the DFT method used in this study was compared with the representative literature about the hydrogen interaction with the anatase TiO\textsubscript{2}(101) surface. As shown in Figure S3, the calculated H\textsubscript{2} desorption energy (1.49 eV) on the anatase TiO\textsubscript{2}(101) agrees well with the one, 1.39 eV, previously reported by Selloni et al.\textsuperscript{30} Figure 3a indicates the calculated reaction pathways for H\textsubscript{2} production on the surfaces of CdS(101) and TiO\textsubscript{1.96C0.04}(101), and the corresponding snapshots are shown in Figure 3b,c. The reaction processes for H\textsubscript{2} generation were composed of following three steps: (1) Two isolated hydrogen atoms gradually became close through the interatomic hopping on the surface, and this atomic migration step did not affect the activation barrier during the entire reaction. (2) The neighboring hydrogen atoms combined to form a H\textsubscript{2} molecule when they were close enough to interact, and this molecularization step was largely endothermic. (3) The formed H\textsubscript{2} molecule was rearranged to settle into the most stable adsorption state, and this molecular migration step required a small amount of energy. We also compared the energy barriers for H\textsubscript{2} production on the CdS(101) and TiO\textsubscript{1.96C0.04}(101). The energy barriers for the H\textsubscript{2} desorption on CdS(101) and TiO\textsubscript{1.96C0.04}(101) were 2.81 and 3.34 eV, respectively. The energy difference between the maximum state and the final state represents the energy required for the rearrangement of hydrogen atoms. These energy differences were 0.09 and 0.31 eV on CdS(101) and TiO\textsubscript{1.96C0.04}(101). It should be noted that a H\textsubscript{2} molecule on CdS(101) needed little energy for the rearrangement during the molecular migration. Consequently, the energy difference before and after the associative desorption of H\textsubscript{2} can be the energy requirement for H\textsubscript{2} production on the CdS(101). The required energy on the TiO\textsubscript{1.96C0.04}(101) was higher than that on CdS(101), indicating that the TiO\textsubscript{1.96C0.04}(101) needed more energy for H\textsubscript{2} production than CdS(101) during the molecularization step. These results explain that H\textsubscript{2} molecules prefer being formed on the CdS surface by Z-schematic charge transfer rather than on the TiO\textsubscript{1.96C0.04} surface by heterojunction assisted charge transfer.

3.3. Electron-Transfer Kinetics. Steady-state and time-resolved PL measurements were carried out in order to investigate the charge-transfer processes of CdS/Au/TiO\textsubscript{1.96C0.04} nanostructure. In these experiments, 1 \textmu{}M rhodamine B (RhB) was used as a tracer dye in order to observe the charge transfer at the solid-state interface. The photoexcited electrons of RhB can be transferred to the CB of TiO\textsubscript{1.96C0.04} and CdS, respectively, leading to a quenching of the PL emission of RhB because the LUMO potential (−1.1 V vs
NHE) of RhB is higher than the CB minimum of TiO$_{1.96}$C$_{0.04}$ and CdS.$^{12}$ Figure 4a shows the steady-state PL spectra of aqueous solutions of RhB in the presence of TiO$_{1.96}$C$_{0.04}$, Au/TiO$_{1.96}$C$_{0.04}$, CdS/TiO$_{1.96}$C$_{0.04}$, CdS/Au/TiO$_{1.96}$C$_{0.04}$, and CdS as a function of emission wavelength with excitation at 405 nm.

The spectra exhibited a peak emission at 580 nm, which is assigned to a radiative recombination of RhB and a weak emission for TiO$_{1.96}$C$_{0.04}$. The CdS has no PL emission at the excitation wavelength (Figure 4b). The colloidal TiO$_{1.96}$C$_{0.04}$ in the RhB solution caused a depression in the peak emission of RhB due to the charge transfer from the excited RhB to the CB of TiO$_{1.96}$C$_{0.04}$ nanoparticles. However, the PL intensity in the range of 500–550 nm was higher than that of pure RhB. This can be attributed to the PL emission of TiO$_{1.96}$C$_{0.04}$ which originates from the oxygen vacancies associated with Ti$^{3+}$ in anatase TiO$_2$.\cite{31,32} The PL emission of RhB was obviously quenched after the Au nanoparticles had been deposited on the surface of TiO$_{1.96}$C$_{0.04}$, indicating that the photoexcited electrons of RhB were transferred to the CB of TiO$_{1.96}$C$_{0.04}$ as well as to the Fermi level of the Au nanoparticles. Furthermore, since the Au nanoparticles absorb at a wavelength of 580 nm, Au/TiO$_{1.96}$C$_{0.04}$ in the absence of RhB could quench up to 50% of the PL emission of TiO$_{1.96}$C$_{0.04}$. The deposition of CdS on the surface of TiO$_{1.96}$C$_{0.04}$ resulted in a measurable suppression of the PL intensity of RhB, and in the absence of RhB, CdS/TiO$_{1.96}$C$_{0.04}$ depressed the PL emission of TiO$_{1.96}$C$_{0.04}$ due to the enhanced charge separation caused by the heterojunction structure. The PL depression of RhB by CdS/TiO$_{1.96}$C$_{0.04}$ was superior to that for Au/TiO$_{1.96}$C$_{0.04}$ at an excitation wavelength of 405 nm, since the CdS was strongly excited at this excitation wavelength. These reasons are explained in detail in the Supporting Information Figure S4a,b. Notably, the PL quenching of RhB by CdS/Au/TiO$_{1.96}$C$_{0.04}$ was more pronounced than that of Au/TiO$_{1.96}$C$_{0.04}$ and CdS/TiO$_{1.96}$C$_{0.04}$ at the excitation wavelength. This enhanced quenching was due to the simultaneous excitation of TiO$_{1.96}$C$_{0.04}$ and CdS shell in the presence of an Au core. The large work function of the Au core permits the excited electrons in the CB of TiO$_{1.96}$C$_{0.04}$ to be captured and then quickly delivers the electrons to the VB of the CdS shell, thereby resulting in an improved charge separation. In the absence of RhB, the quenched PL emission of TiO$_{1.96}$C$_{0.04}$ by CdS/Au/TiO$_{1.96}$C$_{0.04}$ is greater than that by Au/TiO$_{1.96}$C$_{0.04}$ and CdS/TiO$_{1.96}$C$_{0.04}$ over the entire range of the emission wavelength.

Time-resolved PL measurements were performed to further investigate the interfacial charge-transfer kinetics of the CdS/Au/TiO$_{1.96}$C$_{0.04}$ nanostructure where 405 nm laser pulses were used to excite the RhB with TiO$_{1.96}$C$_{0.04}$ and CdS. PL decay traces were collected at a wavelength of 580 nm which consists of the peak emission for RhB and the weak emission for TiO$_{1.96}$C$_{0.04}$. Figure 5 shows the time-resolved PL spectra of the RhB in the presence of TiO$_{1.96}$C$_{0.04}$, Au/TiO$_{1.96}$C$_{0.04}$, CdS/TiO$_{1.96}$C$_{0.04}$, CdS/Au/TiO$_{1.96}$C$_{0.04}$, and CdS. The resulting fluorescence was fitted to the following multiexponential model where the intensity is assumed to be the sum of the individual single-exponential decays$^{33}$

$$I(t) = \sum \frac{A_i}{\tau_i} e^{-t/\tau_i}$$

where $I(t)$ is the fluorescence intensity at time $t$ and $A_i$ and $\tau_i$ are the amplitude and lifetime of the $i$th component, respectively.
In this expression, $A_i$ and $\tau_i$ indicate the amplitude and the decay time of the $i$ component, respectively, and $n$ is the number of individual fluorescence. As shown in Figure 6, decay pathways of the excited electrons in the LUMO of RhB and the CB of TiO$_{1.96}$C$_{0.04}$ were constructed in an attempt to understand the kinetics of the process, based on steady-state PL spectroscopy data. The arrows representing the excitation processes of TiO$_{1.96}$C$_{0.04}$ and CdS were omitted in the charge-transfer models. In the schematic processes, R, T, A, and C denote RhB, TiO$_{1.96}$C$_{0.04}$, Au, and CdS, respectively. $N_R(t)$ and $N_T(t)$ refer to the time-dependent electron populations in the LUMO of RhB and the CB of TiO$_{1.96}$C$_{0.04}$ respectively. All of the fitted parameters are summarized in Table 1. The value of $\chi^2$ was used to judge the goodness-of-fit. Since the CdS has no PL emission at the excitation wavelength, the intensity decay of pure RhB and the RhB in the presence of CdS was found to be a single-exponential function ($n=1$).

However, the decay traces for RhB containing TiO$_{1.96}$C$_{0.04}$ could be fit to a biexponential function ($n=2$) since both RhB and TiO$_{1.96}$C$_{0.04}$ showed the PL emission at 580 nm. The

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

(1)

Figure 5. Time-resolved PL spectra of 1 $\mu$M RhB in the presence of each sample with 405 nm excitation where the emission wavelength is 580 nm.

Figure 6. Decay pathways of the excited electrons in the LUMO of RhB and the CB of TiO$_{1.96}$C$_{0.04}$ when the excitation wavelength is 405 nm. The RhB solution contains (a) none, (b) TiO$_{1.96}$C$_{0.04}$ (c) Au/TiO$_{1.96}$C$_{0.04}$ (d) CdS/TiO$_{1.96}$C$_{0.04}$ (e) CdS/Au/TiO$_{1.96}$C$_{0.04}$ and (f) CdS where R, T, A, and C denote RhB, TiO$_{1.96}$C$_{0.04}$, Au, and CdS, respectively. $N_R(t)$ and $N_T(t)$ refer to the time-dependent electron populations in the LUMO of RhB and the CB of TiO$_{1.96}$C$_{0.04}$ respectively. $k$ represents the rate constant for the charge transfer or charge recombination corresponding to its subscript. The arrows representing the excitation processes of TiO$_{1.96}$C$_{0.04}$ and CdS were omitted in the charge transfer models.

Table 1. Kinetic Parameters Extracted from the Fitted Results of Time-Resolved PL Spectra of 1 $\mu$M RhB in the Presence of Each Sample with Excitation at 405 nm

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<th>entry</th>
<th>$A_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$\chi^2$</th>
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<td>13426.2</td>
<td>1.696</td>
<td></td>
<td></td>
<td>1.000</td>
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<td>RhB + TiO$<em>{1.96}$C$</em>{0.04}$</td>
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<td>6.876</td>
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<td>1.671</td>
<td>135.9</td>
<td>4.209</td>
<td>1.028</td>
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<tr>
<td>RhB + CdS/TiO$<em>{1.96}$C$</em>{0.04}$</td>
<td>12198.7</td>
<td>1.625</td>
<td>230.3</td>
<td>3.717</td>
<td>1.043</td>
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<tr>
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<td>1.596</td>
<td>1626.6</td>
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</table>

The parameters were calculated using the FluoFit software program.
obtained time-resolved PL spectra can be the sum of PL_R (PL of RhB) and PL_T (PL of TiO_{1.96}C_{0.04}). Therefore, the pre-exponential factors A_i can be considered to be the relative contributions of PL_R and PL_T to the obtained time-resolved PL spectra. Furthermore, \( \tau_1 \) in the first exponential term and \( \tau_2 \) in the second exponential term describe the decay times of \( N_R \) and \( N_T \), respectively. Here, differential equations were developed as a charge-transfer model to calculate the rate constants, and these equations are summarized in Table S1. The rate constants in each case were calculated by comparing the exponents of the developed differential equations developed as a charge-transfer model with \( \tau_1 \) extracted from the fitted results of time-resolved PL spectra, and the resulting constants are summarized in Table S2. For example, the recombination rate constant of pure RhB, \( k_R \), was expressed by a reciprocal of \( \tau_1 \) (1.696 ns), and its value was found to be approximately 5.90 \times 10^8 s^{-1}. The RhB in the presence of TiO_{1.96}C_{0.04}, displayed a component of \( \tau_1 \) (1.683 ns) and \( \tau_2 \) (6.876 ns). The short decay time can be a reciprocal of \( k_R + k_{R\to T} \) where \( k_{R\to T} \) was a rate constant for the interfacial charge transfer from the LUMO of RhB to the CB of TiO_{1.96}C_{0.04}, since the \( \tau_1 \) was assigned to the decay of the \( N_R \). Therefore, the value of \( k_{R\to T} \) can be calculated by subtracting a reciprocal of \( \tau_1 \) (1.683 ns) and \( k_R \) and the resulting rate constant was found to be 0.04 \times 10^8 s^{-1}. The long decay time was responsible for the dynamic quenching of TiO_{1.96}C_{0.04}. The recombination rate constant for TiO_{1.96}C_{0.04}, \( k_T \), was represented by a reciprocal of \( \tau_2 \) (6.876 ns). It was estimated to be 1.45 \times 10^8 s^{-1}. The fluorescence decay of RhB in the presence of TiO_{1.96}C_{0.04} was enhanced greater by depositing Au nanoparticles on the TiO_{1.96}C_{0.04} since the photoexcited electrons of RhB were transferred to the CB of TiO_{1.96}C_{0.04} as well as to the Fermi level of Au nanoparticles, \( k_{R\to A} \) (0.04 \times 10^8 s^{-1}). Furthermore, the deposition of Au nanoparticles on the surface of TiO_{1.96}C_{0.04} causes the excited electrons in the CB of TiO_{1.96}C_{0.04} to be entrapped in the Fermi level of Au. This rate constant, \( k_{T\to A} \), was found to be 0.93 \times 10^8 s^{-1}. An obvious depression in the PL intensity of RhB was noted with a deposition of CdS nanoparticles on the surface of TiO_{1.96}C_{0.04} since the photoexcited electrons of RhB transfer to the CB of TiO_{1.96}C_{0.04} and CdS. The excited electrons in the CB of CdS are assumed to be sequentially transferred to the CB of TiO_{1.96}C_{0.04} since CdS emitted only negligible PL. Its corresponding rate constant was denoted by \( k_{R\to C\to T} \) (0.21 \times 10^8 s^{-1}), which was faster than the \( k_{R\to T} \) (0.04 \times 10^8 s^{-1}) and the electron transfer from the LUMO of RhB to the CB of CdS, \( k_{R\to C} \) (0.06 \times 10^8 s^{-1}) due to the heterojunction of TiO_{1.96}C_{0.04} and CdS. The decay of excited electrons in the CB of TiO_{1.96}C_{0.04} to the VB of CdS showed a rate constant, \( k_{T\to C\to T} \), of 1.24 \times 10^8 s^{-1}. When the CdS/Au/TiO_{1.96}C_{0.04} nanostructure was suspended in RhB, the photoexcited electrons of RhB were transferred to the CB of the CdS shell as well as TiO_{1.96}C_{0.04}.

Table 2. Calculated Rate Constants for an Excitation Wavelength of 405 nm

<table>
<thead>
<tr>
<th>entry</th>
<th>rate constants (x10^8 s^{-1})</th>
<th>entry</th>
<th>rate constants (x10^8 s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_R )</td>
<td>5.90</td>
<td>( k_{R\to C} \to T )</td>
<td>0.06</td>
</tr>
<tr>
<td>( k_{R\to T} )</td>
<td>0.04</td>
<td>( k_T )</td>
<td>1.45</td>
</tr>
<tr>
<td>( k_{R\to A} )</td>
<td>0.04</td>
<td>( k_{T\to A} )</td>
<td>0.93</td>
</tr>
<tr>
<td>( k_{R\to C\to A} )</td>
<td>0.21</td>
<td>( k_{T\to C\to A} )</td>
<td>1.24</td>
</tr>
<tr>
<td>( k_{R\to C\to A\to T} )</td>
<td>0.33</td>
<td>( k_{T\to C\to A\to T} )</td>
<td>3.03</td>
</tr>
</tbody>
</table>

Because the Au core interacts strongly with the CdS shell, the electrons which were transferred from the excited RhB to the CB of CdS shell tended to be injected into the excited level of Au core. The electrons injected into Au core can be recombined with the existing holes in the VB of CdS shell where the rate constant, \( k_{R\to C\to A\to T} \), was determined to be 0.33 \times 10^8 s^{-1}. The other electrons, transferred from the excited RhB to the CB of TiO_{1.96}C_{0.04} were injected into the Au core. The injected electrons are likely to decay to the VB of CdS shell, whose rate constant, \( k_{T\to A\to C} \), was 3.03 \times 10^8 s^{-1}. This process showed the fastest electron transfer, leading to an efficient quenching of the holes left in the VB of CdS shell. The calculation result that the \( k_{T\to A\to C} \) was much faster than the \( k_{R\to C\to A\to C} \) verifies the Z-schematic charge transfer of CdS/Au/TiO_{1.96}C_{0.04}. Furthermore, the presence of Au core in the CdS/Au/TiO_{1.96}C_{0.04} nanostructure remarkably facilitated the interfacial charge transfer of TiO_{1.96}C_{0.04} and CdS as compared to CdS/TiO_{1.96}C_{0.04}. These observations explain why the Z-schematic charge transfer of CdS/Au/TiO_{1.96}C_{0.04} results in a high level of H$_2$ production in the visible-light region, as evidenced by the kinetics of the process.

4. CONCLUSIONS

In summary, Z-schematic charge-transfer kinetics at the solid-state interface of CdS/Au/TiO_{1.96}C_{0.04} was demonstrated through the steady-state and time-resolved PL spectroscopies using the RhB as a tracer dye. The electron-transfer processes of photocatalysts were constructed on the basis of the steady-state PL spectra. The rate constants for electron transfer were obtained by correlating the kinetic parameters extracted from the time-resolved PL spectra using the developed differential equations. The PL results revealed that the presence of a Au core, sandwiched between the TiO_{1.96}C_{0.04} and the CdS shell, enabled the excited electrons to be flowed in the reverse direction of the charge transfer of CdS/TiO_{1.96}C_{0.04} heterojunction structure and also accelerated the interfacial charge transfer from TiO_{1.96}C_{0.04} to CdS shell. As a result, the holes left in the VB of CdS were efficiently quenched by the electrons injected from the CB of TiO_{1.96}C_{0.04} through the Au core, contributing to the accumulation of electrons in the CB of CdS shell. The electrons, arrived in the excited state of CdS shell by Z-scheme, possess a strong reducing power due to the high CB minimum (−1.0 V vs NHE) and quickly react with H$^+$ adsorbed at the surface due to the lower energy barrier for the H$_2$ production as compared to the TiO_{1.96}C_{0.04} surface, thereby enhancing H$_2$ production in the range of visible light. This study provides an explanation for why the Z-scheme mechanism of CdS/Au/TiO_{1.96}C_{0.04} is superior to the heterojunction mechanism of CdS/TiO_{1.96}C_{0.04} for H$_2$ production. The findings also offer a novel approach to investigate the kinetic and thermodynamic role of heterointerface in developing the efficient photocatalysts.

ASSOCIATED CONTENT

Supporting Information

Developed differential equations as a charge-transfer model (Table S1), the constructed slabs of TiO_{1.96}C_{0.04}(101) and CdS(101) for DFT calculations (Figure S1), TEM images of CdS/TiO_{1.96}C_{0.04} (Figure S2), DFT-calculated energy path for H$_2$ production on the anatase TiO$_2$(101) (Figure S3), and steady-state PL spectra as a function of excitation wavelength (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.
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Notes
The authors declare no competing financial interest.

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