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Article

Time-resolved infrared spectroscopic investigation of Ga₂O₃ photocatalysts loaded with Cr₂O₃-Rh cocatalysts for photocatalytic water splitting

Qian Ding^{a,b,†}, Tao Chen^{a,c,†}, Zheng Li^a, Zhaochi Feng^a, Xiuli Wang^{a,*}^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, Dalian 116023, Liaoning, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c School of Marine Science and Environment Engineering, Dalian Ocean University, Dalian 116023, Liaoning, China

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ABSTRACT

Investigation of the charge dynamics and roles of cocatalysts is crucial for understanding the reaction of photocatalytic water splitting on semiconductor photocatalysts. In this work, the dynamics of photogenerated electrons in Ga₂O₃ loaded with Cr₂O₃-Rh cocatalysts was studied using time-resolved mid-infrared spectroscopy. The structure of these Cr₂O₃-Rh cocatalysts was identified with high-resolution transmission electron microscopy and CO adsorption Fourier-transform infrared spectroscopy, as Rh particles partly covered with Cr₂O₃. The decay dynamics of photogenerated electrons reveals that only the electrons trapped by the Rh particles efficiently participate in the H₂ evolution reaction. The loaded Cr₂O₃ promotes electron transfer from Ga₂O₃ to Rh, which accelerates the electron-consuming reaction for H₂ evolution. Based on these observations, a photocatalytic water-splitting mechanism for Cr₂O₃-Rh/Ga₂O₃ photocatalysts has been proposed. The elucidation of the roles of the Cr₂O₃-Rh cocatalysts aids in further understanding the reaction mechanisms of photocatalytic water splitting and guiding the development of improved photocatalysts.

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1. Introduction

Photocatalytic overall water splitting is regarded as one of the most promising approaches to convert solar energy into chemical energy in the form of hydrogen [1–13]. Typically, the photocatalysts for photocatalytic overall water splitting consist of the main semiconductor materials and the cocatalysts. The cocatalysts not only enable efficient charge separation at the semiconductor/cocatalyst interface, but also serve as reaction

sites [14–17]. It has been found that loading a Rh-Cr oxide on semiconductor photocatalysts is an effective way to enhance the photocatalytic activity. The core-shell Cr₂O₃-Rh structure on a (Ga_{1-x}Zn_x)(N_{1-x}O_x) photocatalyst reported by Domen et al. [18–20] is one of the most prominent cocatalysts in overall water splitting. When a Rh_{0.5}Cr_{1.5}O₃ cocatalyst was loaded on the Ga₂O₃-based photocatalyst, a quantum yield of 71% was achieved for overall water splitting at 254 nm [21]. Thus far, the strategy of loading the Rh-Cr oxide cocatalyst has been ap-

* Corresponding author. Tel: +86-411-84379027; Fax: +86-411-84694447; E-mail: xiuliwang@dicp.ac.cn

† These authors equally contributed to the work.

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plied to many photocatalytic systems such as $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ [18–20,22–25], Ga_2O_3 [21,26–29], SrTiO_3 [30–32], and $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ [33,34].

To date, much effort has been devoted to understanding how Rh–Cr oxide cocatalysts work. Rh–Cr oxide cocatalysts are generally considered as electron sinks, and are proven to be the active sites for proton reduction by control experiments using Ag^+ as an electron scavenger [35]. For the core-shell Cr_2O_3 –Rh cocatalyst, it has been demonstrated that the Rh nanoparticles (core) act as the H_2 evolution center, while the Cr_2O_3 component (shell) suppresses the back-reaction between H_2 and O_2 by preventing the permeation of O_2 [18–20,36]. Maeda et al. [37] proposed that the co-loading of Cr_2O_3 with Rh_2O_3 presumably changes the electronic state and chemical properties of the Rh_2O_3 cocatalyst, and the migration of the photogenerated electrons to the Rh_2O_3 cocatalyst and/or the reduction of surface-adsorbed H^+ followed by H_2 formation proceed more smoothly. Recently, Phivilay et al. [38] reported that the dispersed RhO_x species (H_2 evolution center) exists on both the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ support and the CrO_x nanoparticles in the $(\text{Rh}_{2-y}\text{Cr}_y\text{O}_3)/(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ photocatalyst, and the CrO_x species appears to facilitate electron transfer from the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ support to the RhO_x species. Considerable efforts have been invested in revealing the roles of Rh–Cr oxide cocatalysts for photocatalytic water splitting; however, their nature is still not fully understood. Particularly, information on how these cocatalysts affect the dynamics of photogenerated charge carriers in the photocatalysts is limited.

In this work, the decay dynamics of photogenerated electrons in Ga_2O_3 photocatalysts loaded with Cr_2O_3 –Rh cocatalysts was investigated by microsecond time-resolved mid-infrared (MIR) spectroscopy (TR-MIR). The electron decay dynamics was monitored in vacuum or in the presence of H_2O or O_2 to reveal the roles of Rh or the Cr_2O_3 –Rh cocatalysts in photocatalytic water splitting. A reaction mechanism of photocatalytic water splitting on the Cr_2O_3 –Rh/ Ga_2O_3 photocatalysts was proposed.

2. Experimental

2.1. Catalyst synthesis

The Ga_2O_3 photocatalyst was prepared by an ammonia precipitation method [28]. First, the $\text{Ga}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ reagent was dissolved in deionized water to form a $\text{Ga}(\text{NO}_3)_3$ solution (6 wt%). The hydroxylation of this solution was then carried out by dripping a 3 wt% ammonia solution under vigorous stirring at room temperature until the supernatant solution attained a pH of 9. Finally, the produced hydroxide was calcined at 1173 K for 6 h to obtain the Ga_2O_3 photocatalyst. The Ga_2O_3 photocatalyst with 0.5 wt% Rh loading, $\text{Rh}/\text{Ga}_2\text{O}_3$, was prepared by photodeposition, where a certain amount of the Ga_2O_3 photocatalyst was dispersed into a Na_3RhCl_6 solution of appropriate concentration, following which the suspension was irradiated by a 450 W Hg lamp (USHIO UM452) for 4 h. The Cr_2O_3 -loaded Ga_2O_3 photocatalyst, $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$ (0.75 wt% Cr), was prepared by dispersing the Ga_2O_3 support into a K_2CrO_4 solution and

then irradiated by the 450 W Hg lamp for 4 h. The Cr_2O_3 –Rh-loaded Ga_2O_3 photocatalyst, Cr_2O_3 –Rh/ Ga_2O_3 (0.5 wt% Rh and 0.75 wt% Cr), was synthesized by loading Rh (0.5 wt%) first and then Cr_2O_3 (0.75 wt% Cr) on the Ga_2O_3 photocatalyst using the same photodeposition method.

2.2. Characterizations of catalysts

The ultraviolet-visible (UV-Vis) spectra were collected with a Shimadzu UV 2550 spectrophotometer. X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max-2500/PC powder diffractometer ($\text{Cu } K_\alpha$ radiation) with an operating voltage of 40 kV and operating current of 200 mA. A scan rate of $5^\circ/\text{min}$ was applied at a step size of 0.02° . The high-resolution transmission electron microscopy (HRTEM) images were obtained on an FEI TECNAI F30 S-Twin microscope. The X-ray photoelectron spectra were obtained on an X-ray photoelectron spectroscopy (XPS) instrument (Thermo Fisher Scientific K-Alpha, Al). The steady-state photoluminescence (PL) spectra were collected on a fluorescence spectrometer (QM400, Xe lamp, 250 nm excitation).

The *in situ* Fourier-transform infrared (FT-IR) spectra for CO adsorption were collected on a Nicolet Nexus 470 IR spectrometer with a DTGS detector. The sample (~ 30 mg) was pressed into a self-supporting wafer. Before the measurement, each catalyst wafer inside the *in situ* IR cell was pretreated at 473 K under a flowing H_2 atmosphere (20 mL/min) for 1 h. After cooling to room temperature, the IR cell was evacuated for 60 min. Subsequently, ~ 25 Torr CO was introduced into the IR cell followed by the evacuation of gaseous CO. The IR spectra of CO adsorption were collected by averaging 32 scans at a resolution of 4 cm^{-1} , and the spectrum captured before CO adsorption was used as the background.

2.3. Photocatalytic reactions

The photocatalytic water-splitting reaction was performed in an inner irradiation quartz cell connected with a closed gas circulation system. The photocatalyst powder (0.1 g) was dispersed in well-outgassed water (500 mL) under vigorous stirring by a magnetic stirrer. The light source was a 450 W high-pressure mercury lamp and its emission spectrum is shown in Fig. S1. The reaction temperature was maintained at 287 ± 1 K. The amount of evolved H_2 was determined by online gas chromatography (Shimadzu; GC-8A).

2.4. Time-resolved MIR spectroscopy (TR-MIR)

For the time-resolved MIR spectroscopic study, the photocatalyst was coated on a BaF_2 plate to form a thin film ($\sim 4 \text{ mg}/\text{cm}^2$) [39], and the catalyst film was mounted in a quartz IR cell equipped with BaF_2 windows. The IR cell was connected to a vacuum system at 10^{-3} Torr. Water vapor was introduced in the IR cell through the vacuum system and oxygen was introduced in the cell by purging O_2 gas. The three-dimensional time-resolved IR absorption spectra were collected on a Nicolet 870 step-scan FT-IR spectrometer equipped with a

fast-response MCT detector (20 MHz). The AC output of the MCT (20 MHz–110 Hz), amplified by a factor of 50 with an SR560 preamplifier (1 MHz to 0.03 Hz), was used to measure the transient signals [40]. The static background was measured by the DC output (20 MHz–0 Hz) of the MCT detector. A pulse of 266 nm light with 6–8 ns width from a Q-switched Nd:YAG laser (Spectra-Physics) was used to excite the photocatalysts. The repetition rate and energy of the laser pulse was set to 1 Hz and ~ 1.5 mJ/pulse, respectively. Synchronization between laser excitation and data acquisition was achieved with a Stanford Research model DG 535 pulse generator.

A modified measurement mode [40] was used to directly monitor the decay dynamics of an average IR absorption (1000–4000 cm^{-1}) at room temperature in either vacuum, or in the presence of water vapor (12.5 Torr) or O_2 gas (1 atm). In this measurement mode, the stepping mirror was fixed at a position. The DC output (20 MHz–0 Hz) of the MCT, amplified by a factor of 50 with an SR560 preamplifier (1 MHz to 0.03 Hz), was used to measure the transient signals that were then accumulated and averaged in an external oscilloscope (Tektronix, TDS5104). Before measuring the transient signals, $\Delta I(t)$, the DC output of the MCT with no amplification modulated by a handmade chopper was used to measure the intensity (I) of the entire IR light in the 1000–4000 cm^{-1} range, and the average transient absorbance changes were calculated as $\Delta A(t) = -\log\{[I + \Delta I(t)/50]/I\}$.

3. Results and discussion

3.1. Photocatalytic activity

The photocatalytic activities for overall H_2O splitting on the Ga_2O_3 -based photocatalysts were evaluated (Fig. 1). H_2 and O_2 in a molar ratio of approximately 2:1 were observed on the $\text{Rh}/\text{Ga}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-Rh}/\text{Ga}_2\text{O}_3$ photocatalysts, while evolved H_2 and evolved O_2 occurred in a higher molar ratio than 2:1 for the Ga_2O_3 and $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$ photocatalysts. The Ga_2O_3 photocatalyst exhibited very low photocatalytic activity for overall water splitting. After the introduction of H_2 evolution sites by loading the Rh cocatalyst on the Ga_2O_3 photocatalyst, the activ-

ity increased by a factor of ~ 6 . The catalytic activity increased by a factor of ~ 2 when the Cr_2O_3 cocatalyst was loaded on the Ga_2O_3 support. Interestingly, when both Cr_2O_3 and Rh were co-loaded on the Ga_2O_3 photocatalyst, the activity increased by a factor of ~ 18 .

3.2. Structure and morphology

The XRD patterns of the as-prepared Ga_2O_3 and $\text{Cr}_2\text{O}_3\text{-Rh}/\text{Ga}_2\text{O}_3$ photocatalysts are shown in Fig. S2. Almost identical XRD patterns were observed for these two photocatalysts, and all the diffraction peaks were assigned to those of β -phase Ga_2O_3 . No distinct diffraction peaks of Cr_2O_3 or Rh (Rh_2O_3) were observed for the $\text{Cr}_2\text{O}_3\text{-Rh}/\text{Ga}_2\text{O}_3$ photocatalyst, which may be due to the low loading quantity and low crystallinity of these cocatalysts. The optical band gap determined by UV-Vis spectroscopy (Fig. S3) for Ga_2O_3 , $\text{Rh}/\text{Ga}_2\text{O}_3$, and $\text{Cr}_2\text{O}_3\text{-Rh}/\text{Ga}_2\text{O}_3$ was approximately 4.5 eV, indicating that the optical band gap of bulk Ga_2O_3 was essentially unperturbed by the deposition of the Rh or $\text{Cr}_2\text{O}_3\text{-Rh}$ cocatalysts. The bulk Ga_2O_3 dominated the absorption properties of the cocatalyst-loaded Ga_2O_3 photocatalysts. The XPS profiles in the Cr 2p and Rh 3d regions of the $\text{Cr}_2\text{O}_3\text{-Rh}/\text{Ga}_2\text{O}_3$ photocatalyst are shown in Fig. S4. The Cr $2p_{3/2}$ peak at 576.6 eV was in good agreement with the value (576.7 eV) for Cr_2O_3 , and the Rh $3d_{5/2}$ peak at 309.6 eV was also observed, which indicates the successful loading of Cr_2O_3 and Rh on the Ga_2O_3 surface [23].

To understand the roles of the Rh and Cr_2O_3 cocatalysts, the morphology of $\text{Cr}_2\text{O}_3\text{-Rh}/\text{Ga}_2\text{O}_3$ was characterized by high-resolution TEM. As shown in Fig. 2, the lattice fringes with distance $d = 0.3$ nm corresponding to the facets of Ga_2O_3 and distance $d = 0.23$ nm agreeing well with the {111} facets of Rh can be clearly seen. However, no lattice fringes of Cr_2O_3 were observed in the $\text{Cr}_2\text{O}_3\text{-Rh}/\text{Ga}_2\text{O}_3$ photocatalyst, which may be due to the high dispersion or the low crystallinity of Cr_2O_3 on the Ga_2O_3 surface. This result was different from that in the HRTEM images of $\text{Cr}_2\text{O}_3/\text{Rh}/(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, in which a core-shell structure (Rh is covered by Cr_2O_3) was formed on $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ [20].

To reveal whether the Cr_2O_3 cocatalyst covered the surface

Fig. 1. Photocatalytic activities of the photocatalysts. 0.1 g photocatalyst was dispersed into 500 mL deionized water and irradiated with a 450 W mercury lamp.

Fig. 2. HRTEM images of $\text{Cr}_2\text{O}_3\text{-Rh/Ga}_2\text{O}_3$ photocatalysts. (a) lattice fringes corresponding to Ga_2O_3 ; (b) lattice fringes corresponding to Rh.

of Rh particles in the $\text{Cr}_2\text{O}_3\text{-Rh/Ga}_2\text{O}_3$ photocatalyst, the adsorption of CO probe molecules on the $\text{Rh/Ga}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3\text{-Rh/Ga}_2\text{O}_3$ photocatalysts was investigated by FT-IR spectroscopy and the results are shown in Fig. 3. In the case of $\text{Rh/Ga}_2\text{O}_3$, the spectrum shows three bands at 2092, 2055, and 2021 cm^{-1} . The bands at 2092 and 2021 cm^{-1} can be assigned to the symmetric and antisymmetric CO stretching modes of an isolated $\text{Rh}^{\text{I}}(\text{CO})_2$ species, respectively [41]. The band at 2055 cm^{-1} was assigned to a species of CO linear-bonded to Rh^0 atoms [41]. It has been reported that no CO is absorbed on Cr_2O_3 at room temperature [42–44]. After loading Cr_2O_3 on $\text{Rh/Ga}_2\text{O}_3$, the peaks corresponding to the species of CO adsorbed on Rh at 2092, 2055, and 2021 cm^{-1} decrease dramatically but still exist, indicating that the cocatalyst of Rh was partly covered with Cr_2O_3 in the $\text{Cr}_2\text{O}_3\text{-Rh/Ga}_2\text{O}_3$ photocatalyst.

3.3. Decay dynamics of photogenerated electrons in Ga_2O_3 -based photocatalysts

To further study the roles of the Rh and Cr_2O_3 cocatalysts in Ga_2O_3 -based photocatalysts, time-resolved MIR spectroscopy was employed to observe the decay dynamics of photogenerated electrons. Fig. 4 shows the time-resolved MIR absorption spectra of $\text{Rh/Ga}_2\text{O}_3$ in air that was recorded in a step-scan measurement mode. A broad MIR absorption appeared, and the absorption monotonously increased in intensity with lower

Fig. 3. FT-IR spectra of CO adsorbed on $\text{Rh/Ga}_2\text{O}_3$ (1) and $\text{Cr}_2\text{O}_3\text{-Rh/Ga}_2\text{O}_3$ (2) photocatalysts.

Fig. 4. Time-resolved IR absorption spectra of $\text{Rh/Ga}_2\text{O}_3$ in air recorded in the step-scan measurement mode. A 1 Hz, 266 nm laser was used to excite the sample. The inset shows the normalized decay curves at 1480, 1300, and 900 cm^{-1} .

wavenumbers. The transient MIR absorption spectra obey the equation $\Delta\text{Absorbance} = A\tilde{\nu}^{-p}$, where A is a constant, $\tilde{\nu}$ is the wavenumber, and p is the scattering constant [45–48]. The value of p fitted from the absorption spectra was 1.8. A value of $p = 1.5$ is expected for the conservation of electron momentum with acoustic phonons in an indirect semiconductor. Higher values of p are due to coupling with optical phonons ($p = 2.5$) or ionized impurities ($p = 3\text{--}3.5$), or both [49]. Thus, the transient MIR absorption is assigned to the intraband transitions of conduction band (CB) electrons or the excitation of shallowly trapped electrons to the CB of Ga_2O_3 [50,51]. These results indicate that the transient absorption decay dynamics should be independent of any wavenumber. As shown in the inset of Fig. 4, the decay curves at 990, 1300, and 1480 cm^{-1} are identical after normalization. Thus, it was reasonable to investigate the electron decay dynamics by monitoring the time profile of the average IR absorption (1000–4000 cm^{-1}).

Fig. 5 shows the transient MIR absorbance changes of Ga_2O_3 measured in vacuum and in the presence of water vapor (12.5 Torr) and O_2 gas (1 atm). The decay of the absorbance change

Fig. 5. Transient MIR absorption decays of Ga_2O_3 in vacuum (1), water vapor (2), and oxygen (3) excited by a 1 Hz, 266 nm laser pulse. The inset shows the normalized transient MIR absorption profiles.

Table 1

Lifetimes ($\tau_{50\%}$) of Ga₂O₃-based photocatalysts in vacuum, water vapor, and O₂.

$\tau_{50\%}/\mu\text{s}$	in vacuum	in H ₂ O	in O ₂
Ga ₂ O ₃	31	31	31
Cr ₂ O ₃ /Ga ₂ O ₃	31	53	31
Rh/Ga ₂ O ₃	21	12	21
Cr ₂ O ₃ -Rh/Ga ₂ O ₃	12	10	12

$\tau_{50\%}$ (the time in which the absorbance change decays by 50%) reflects the dynamics of charge recombination and electron-consumed reaction in the measured microsecond to millisecond time range.

corresponds to the decay of the photogenerated electrons in the Ga₂O₃ photocatalyst. When the catalyst was measured in vacuum, the decay process was ascribed to the slow electron-hole recombination in bulk Ga₂O₃, and the lifetime ($\tau_{50\%}$, the time in which the absorbance change decays by 50%) of these electrons was approximately 31 μs (Table 1). The electrons observed in these microsecond time-resolved experiments are long-lived electrons that successfully survived from the fast electron-hole recombination in the pre-microsecond timescale (within the initial time delay of 4 μs in our experiments). We previously reported that the long-lived electrons in TiO₂-based [40] and Ga₂O₃-based [51] photocatalysts should participate in the H₂ evolution reaction. Thereafter, the electron dynamics was investigated in the presence of water vapor. The decay curve was almost identical to that obtained in vacuum and indicated that these long-lived electrons cannot efficiently react with the surface-adsorbed water, which was in agreement with the low activity of photocatalytic water splitting on Ga₂O₃ in absence of any cocatalysts. The effect of O₂ on electron dynamics was further investigated to understand the reactivity of the photoelectrons of Ga₂O₃ photocatalysts. The initial absorbance change increased by 41.9% when the catalyst was exposed to O₂, which might be due to the electron accumulation caused by the hole transfer from Ga₂O₃ to an O₂-derived adsorbate, ozonide, in the pre-microsecond timescale [52]. Independent of the surrounding atmosphere, Ga₂O₃ exhibits almost identical electron decay lifetimes as shown in the normalized decays in the inset of Fig. 5 and Table 1, indicating that photocatalytic water or the oxygen reduction reaction can hardly occur on the Ga₂O₃ semiconductor surface without any cocatalyst.

The decay curves of the photoinduced electrons in the Cr₂O₃/Ga₂O₃ photocatalyst are shown in Fig. 6. The initial absorbance change of Cr₂O₃/Ga₂O₃ in vacuum decreased to approximately 71.5% of that of Ga₂O₃, but the lifetime of photogenerated electrons remained at approximately 31 μs . The initial absorbance change of Cr₂O₃/Ga₂O₃ in the presence of water vapor or oxygen decreased further by 10.4% or 20.7%, respectively, relative to that of Ga₂O₃ in vacuum, whereas the electron life of Cr₂O₃/Ga₂O₃ increased to 53 μs in water vapor and remained at 31 μs in oxygen. Although the initial absorbance changes of Cr₂O₃/Ga₂O₃ decrease relative to those of Ga₂O₃, the electron life remained the same in vacuum or oxygen, and even increased in water vapor. Therefore, the Cr₂O₃ cocatalyst should not be the recombination centers; otherwise, the initial absorbance change and the electron lifetimes would decrease

Fig. 6. Transient MIR absorption decays of Cr₂O₃/Ga₂O₃ in vacuum (1), water vapor (2), and oxygen (3) excited by a 1 Hz, 266 nm laser pulse. The inset shows the normalized transient MIR absorption profiles.

simultaneously. Considering that the photocatalytic activity of Cr₂O₃/Ga₂O₃ was slightly higher than that of only Ga₂O₃, the decrease in the initial absorbance change was attributed to the efficient electron transfer from Ga₂O₃ to Cr₂O₃ but not to the faster electron-hole recombination in the pre-microsecond timescale. Nevertheless, this assignment was based on the premise that the electrons trapped in Cr₂O₃ did not contribute to the MIR absorption, or the extinction coefficient of the electrons trapped in Cr₂O₃ for MIR adsorption was less than those in Ga₂O₃. The probable reason behind the increased lifetime of the electrons in Cr₂O₃/Ga₂O₃ measured in water vapor was that the water oxidation (hole-consuming process) on Ga₂O₃ was promoted by the loaded Cr₂O₃, following which electron-hole recombination was impeded.

The initial absorbance change of Rh/Ga₂O₃ in vacuum increased by a factor of ~1.5 to that of Ga₂O₃ (Fig. 7), which is opposite to the result of the electron transfer from Ga₂O₃ to Rh in a pre-microsecond timescale. The increase in the initial absorbance change suggested that the fast electron-hole recombination in Rh/Ga₂O₃ in the pre-microsecond timescale was

Fig. 7. Transient MIR absorption decays of Rh/Ga₂O₃ in vacuum (1), water vapor (2), and oxygen (3) excited by a 1 Hz, 266 nm laser pulse. The inset shows the normalized transient MIR absorption profiles.

retarded, which might be ascribed to the surface passivation of Ga_2O_3 and the reduction of ultrafast recombination centers caused by Rh loading. The initial absorbance change of Rh/ Ga_2O_3 with the introduction of water vapor or oxygen reduced by 25.8% or 19.6%, respectively, relative to that in vacuum, probably owing to the capture of electrons by the surface-adsorbed water or oxygen in the pre-microsecond timescale. In the presence of water vapor, the lifetime of electrons in the Rh/ Ga_2O_3 photocatalyst was shortened to 12 μs – approximately half of that in vacuum. The accelerated decay in the tens-of-microsecond timescale was attributed to the water/proton reduction reaction (electron-consuming process). It has been reported that the time scale of the water/proton reduction reaction on Pt/ TiO_2 is in the order of microseconds [53], so it is reasonable to attribute the accelerated electron decay in the order of microseconds to the water/proton reduction reaction (hydrogen generation reaction). As the photogenerated electrons in Ga_2O_3 had no reactivity toward water reduction, they efficiently participated in water reduction via Rh nanoparticles. The lifetime of the photogenerated electrons in Rh/ Ga_2O_3 measured in vacuum was approximately 21 μs , which was much shorter than that measured for Ga_2O_3 (31 μs) under the same conditions. This accelerated electron decay was attributed to the water reduction reaction because even when we measured in vacuum (10^{-3} Torr), a small amount of water was inevitably adsorbed on the catalyst and reacted with the electrons via the Rh cocatalyst.

When Rh and Cr_2O_3 were stepwise-deposited on Ga_2O_3 , the initial absorbance change of Cr_2O_3 -Rh/ Ga_2O_3 in vacuum decreased to approximately half of that of Ga_2O_3 (Fig. 8), and approximately 65.7% lower relative to Rh/ Ga_2O_3 . For the similar reasons discussed above, the decrease in the initial absorbance change could not be ascribed to the faster recombination of the charge carriers within 4 μs , but was ascribed to the more efficient electron transfer in the pre-microsecond timescale from Ga_2O_3 to the Cr_2O_3 -Rh cocatalyst than that from Ga_2O_3 to the Rh cocatalyst in the Rh/ Ga_2O_3 photocatalyst. The lifetime of electrons of Cr_2O_3 -Rh/ Ga_2O_3 in vacuum was ~ 12 μs , which is no-

Fig. 8. Transient MIR absorption decays of Cr_2O_3 -Rh/ Ga_2O_3 in vacuum (1), water vapor (2), and oxygen (3) excited by a 1 Hz, 266 nm laser pulse. The inset shows the normalized transient MIR absorption profiles.

ticeably shorter than that of Ga_2O_3 (~ 31 μs) or Rh/ Ga_2O_3 (~ 21 μs). It can be seen that for the Ga_2O_3 , Rh/ Ga_2O_3 , and Cr_2O_3 -Rh/ Ga_2O_3 photocatalysts measured in vacuum, the decay rates of the long-lived electrons correlate well with their activities of photocatalytic overall water splitting. The faster decay of the long-lived electrons in the Cr_2O_3 -Rh/ Ga_2O_3 photocatalyst can be explained by the faster reaction between the long-lived electrons and the small amount of surface-adsorbed water via the Rh cocatalyst. It has been reported that the role of Cr_2O_3 in a Cr_2O_3 -Rh cocatalyst is to suppress the back-reaction [36]. Besides this function of Cr_2O_3 , here we report another function of Cr_2O_3 on the basis of time-resolved IR absorption measurement results: to promote electron transfer from Ga_2O_3 to the Rh particles. This conclusion was also supported by the steady-state PL measurements (Fig. S5). The promotion effect may be mainly due to the structural modification of Rh by Cr_2O_3 revealed by the IR results with the CO probe. Moreover, the trapped electrons in Cr_2O_3 may transfer to the Rh nanoparticles, either directly or indirectly by transferring back to Ga_2O_3 and then transfer to Rh eventually. The promotion of electron transfer from $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ to RhO_x species by Cr_2O_3 in the $(\text{Rh}_{2-y}\text{Cr}_y\text{O}_3)/(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ photocatalyst was reported by Phivilay et al. [38], and a similar mechanism for the Ni- $\text{NiS}_x/\text{TiO}_2$ photocatalysts that the Ni cocatalyst mediates the electron transfer from TiO_2 to NiS_x was also proposed [54]. The initial absorbance reduced further with the introduction of water or oxygen by 14.2% or 17.2%, respectively, than that in vacuum, which may be attributed to electron capture by water vapor and oxygen in the pre-microsecond timescale. The lifetime of electrons of Cr_2O_3 -Rh/ Ga_2O_3 in water vapor was further shortened to ~ 10 μs . The decay rates of the long-lived electrons in the Ga_2O_3 , Rh/ Ga_2O_3 , and Cr_2O_3 -Rh/ Ga_2O_3 photocatalysts measured in water vapor also exhibited the same trend with the photocatalytic activities of these photocatalysts.

The photogenerated electron dynamics of the Ga_2O_3 -based photocatalysts are summarized in Table 1. In vacuum, the loading of Rh or Cr_2O_3 -Rh accelerated the decay of the long-lived electrons in Ga_2O_3 , whereas the loading of Cr_2O_3 did not change the electron decay dynamics. For Cr_2O_3 -Rh/ Ga_2O_3 , the drastically reduced initial absorbance change and the shortened electron life relative to those of $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$ and Rh/ Ga_2O_3 indicated that the Cr_2O_3 modification improved the electron transfer from Ga_2O_3 to Rh nanoparticles. In water vapor, the electron life of Rh/ Ga_2O_3 and Cr_2O_3 -Rh/ Ga_2O_3 decreased relative to those in vacuum, indicating that the electrons on Rh participated efficiently in the hydrogen production reaction on Rh/ Ga_2O_3 and Cr_2O_3 -Rh/ Ga_2O_3 . In O_2 atmosphere, the hole transfer from Ga_2O_3 to an O_2 -induced adsorbate, ozonide, in the pre-microsecond timescale, was considered to cause an increase in the initial absorbance of Ga_2O_3 in O_2 ; however, after loading the cocatalysts, no such enhancement effects were observed, suggesting that the adsorption of O_2 was inhibited by the cocatalysts.

Based on the above results and discussion, the reaction mechanisms for photocatalytic overall water splitting on Cr_2O_3 -Rh/ Ga_2O_3 are proposed in Scheme 1 and Fig. S6. After light excitation, photogenerated electrons in Ga_2O_3 transferred

Scheme 1. Schematic model of working mechanisms of Rh or Rh-Cr₂O₃ in photocatalytic water splitting on Rh/Ga₂O₃ or Cr₂O₃-Rh/Ga₂O₃. Blue arrows indicate the photocatalytic redox reactions. Black arrows indicate the photogenerated charge transfer processes. The thickness of the black solid arrow lines indicates the relative contents of the transfer path, where thicker arrow lines represent higher content than the thinner ones. The dashed lines indicate the possible charge transfer.

to the loaded cocatalysts. Rh nanoparticles served as the active sites for hydrogen production, whereas oxygen evolution occurred on the Ga₂O₃ surface. Regarding the roles of Cr₂O₃, the rates of electron transfer from Ga₂O₃ to Rh were promoted efficiently by Cr₂O₃ modification, which considerably enhanced the photocatalytic H₂ evolution reaction. The promoted electron transfer occurred predominately due to the structural modification of Rh by Cr₂O₃. On the other hand, cocatalyst loading could effectively inhibit the adsorption of oxygen on the Ga₂O₃ surface, which helped to promote water oxidation on the Ga₂O₃ surface.

4. Conclusions

In this work, the stepwise photodeposition of Rh and Cr₂O₃ cocatalysts on Ga₂O₃ was performed, and the electron decay dynamics of these photocatalysts for photocatalytic water splitting was studied by time-resolved MIR spectroscopy. The long-lived electrons in Ga₂O₃ had low reactivity toward water reduction, and only the electrons trapped by Rh participated in the H₂ evolution reaction. Co-loading of Cr₂O₃ efficiently promoted the electron transfer from Ga₂O₃ to Rh, which consider-

ably enhanced the photocatalytic H₂ evolution. The functions of the Cr₂O₃-Rh cocatalysts for photocatalytic water splitting on the Ga₂O₃-based photocatalysts were thus proposed, deepening the understanding of the role of cocatalysts on metal oxide photocatalysts.

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Graphical Abstract

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Time-resolved infrared spectroscopic investigation of Ga₂O₃ photocatalysts loaded with Cr₂O₃-Rh cocatalysts for photocatalytic water splitting

Qian Ding, Tao Chen, Zheng Li, Zhaochi Feng, Xiuli Wang*
Dalian Institute of Chemical Physics, Chinese Academy of Sciences;
University of Chinese Academy of Sciences; Dalian Ocean University

The working mechanisms of Cr₂O₃-Rh cocatalysts are proposed for photocatalytic water splitting on Ga₂O₃-based photocatalysts. Co-loading of Cr₂O₃ efficiently promotes electron transfer from Ga₂O₃ to Rh, which considerably enhances the photocatalytic H₂ evolution.

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Cr₂O₃-Rh/Ga₂O₃光催化分解水的时间分辨红外光谱研究

丁倩^{a,b,†}, 陈涛^{a,c,†}, 李政^a, 冯兆池^a, 王秀丽^{a,*}

^a中国科学院大连化学物理研究所, 催化基础国家重点实验室, 辽宁大连116023

^b中国科学院大学, 北京100049

^c大连海洋大学, 海洋科技与环境学院, 辽宁大连116023

摘要: 研究半导体光催化分解水反应中光生电荷动力学和助催化剂的作用对理解其反应机理至关重要。一般来说, 助催化剂不仅可以促进半导体/助催化剂界面处的光生电荷高效分离, 而且可以作为反应活性中心来直接催化表面氧化或还原反应。Cr₂O₃-Rh是一种重要的产氢助催化剂, 通过负载Cr₂O₃-Rh助催化剂来提高光催化分解水的策略被应用到许多光催化分解水体系中。已有研究发现, Rh/Cr₂O₃核壳结构助催化剂的产氢活性位仍然在Rh纳米粒子表面, 而Cr₂O₃壳层阻止O₂到达Rh核从而抑制生成水的逆反应。此外, 在(Rh_{2-y}Cr_yO₃)/(Ga_{1-x}Zn_x)(N_{1-x}O_x)光催化剂中, CrO_x促进了从半导体光催化剂到活性位RhO_x的电子转移。然而, Cr₂O₃-Rh助催化剂的作用本质(包括Cr₂O₃所起的作用)仍然是一个悬而未决的问题, 特别是Cr₂O₃-Rh助催化剂的负载对半导体催化剂中光生电荷动力学影响的研究还非常少。

本文采用原位光沉积的方法制备了Ga₂O₃、Rh/Ga₂O₃、Cr₂O₃/Ga₂O₃和Cr₂O₃-Rh/Ga₂O₃等一系列光催化剂; 采用紫外可见漫反射光谱(UV-Vis DRS)、X射线光电子能谱(XPS)、CO吸附红外光谱和高分辨透射电镜(HRTEM)等表征手段研究了Cr₂O₃-Rh助催化剂的结构和形貌; 采用时间分辨红外光谱(TR-MIR)研究了这些光催化剂在真空或者反应物(水汽或者氧气)存在条件下的光生电子的衰减动力学过程。

UV-Vis DRS结果表明, Ga₂O₃的带隙基本上不受Rh或者Cr₂O₃-Rh助催化剂负载的影响。XPS结果表明, Cr₂O₃和Rh成功

地担载在 Ga_2O_3 表面上。CO吸附红外和HRTEM结果表明,在 Cr_2O_3 -Rh助催化剂中Rh纳米粒子被 Cr_2O_3 部分覆盖。光生电子的衰减动力学研究结果显示, Ga_2O_3 中光生电子很难直接参与质子还原反应,只有被Rh捕获后的电子才能高效地参与产氢反应;在水汽存在条件下 Ga_2O_3 、 $\text{Rh}/\text{Ga}_2\text{O}_3$ 和 Cr_2O_3 - $\text{Rh}/\text{Ga}_2\text{O}_3$ 中光生电子的衰减速率随着它们光催化产氢活性的升高而增加;与 $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$ 和 $\text{Rh}/\text{Ga}_2\text{O}_3$ 相比, Cr_2O_3 - $\text{Rh}/\text{Ga}_2\text{O}_3$ 中光生电子的初始吸光度和寿命均减小,说明 Cr_2O_3 对 $\text{Rh}/\text{Ga}_2\text{O}_3$ 的结构修饰促进了电子从 Ga_2O_3 向Rh的转移过程,从而加速了质子还原反应。最后,基于这些结果提出了 Cr_2O_3 - $\text{Rh}/\text{Ga}_2\text{O}_3$ 光催化剂上的光催化分解水机理。本文的研究结果有利于更加深入地认识半导体光催化分解水反应机理,并为高效半导体光催化剂的合成提供一定的理论支持和指导。

关键词: 光催化; 时间分辨红外光谱; 光生电荷动力学; 全分解水; 助催化剂; 氧化镓

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*通讯联系人. 电话: (0411)84379027; 传真: ((0411)84694447; 电子信箱: xiuliwang@dicp.ac.cn

[†]共同第一作者

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