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Study of visible-light-induced interfacial charge excitation and its photocatalytic activities

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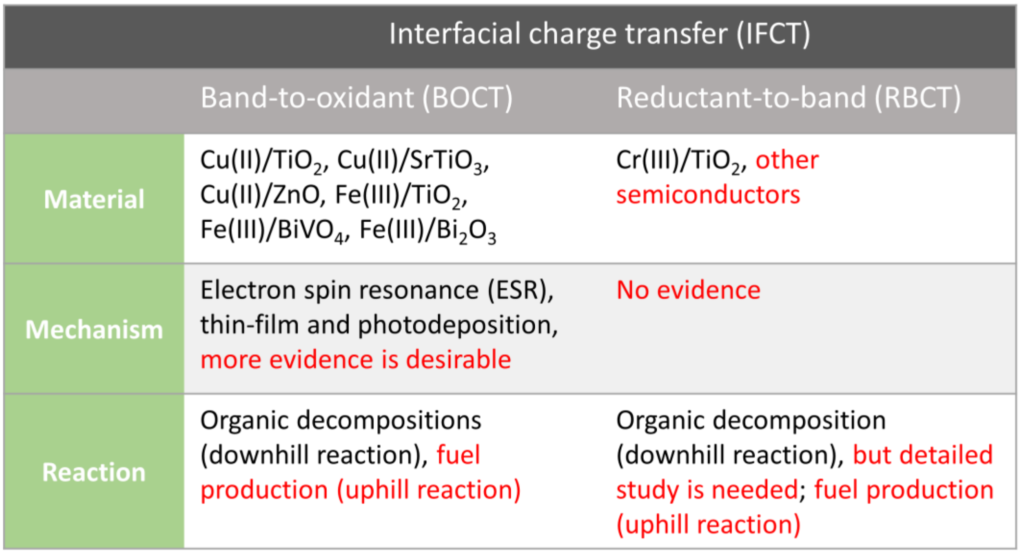
Dissertation Outline

Chapter 1. Introduction

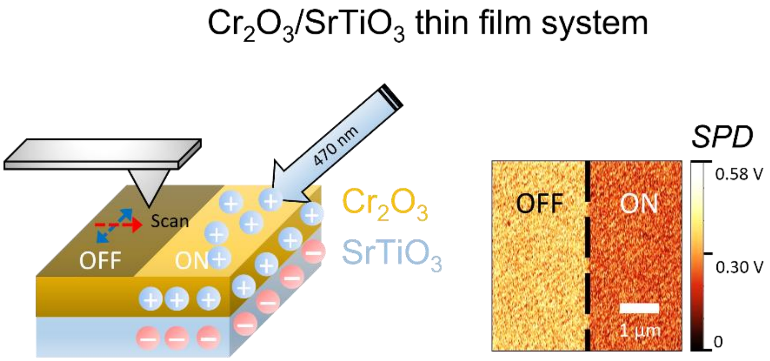
The solar spectrum comprises 46% of visible-light, from which the radiation intensity is the highest compared to that of UV (7%). Energy harvesting from visible solar light or an indoor illuminant is necessary for practical photocatalysis. However, efficient and stable photocatalysts are mostly wide-gap semiconductors (*e.g.*, TiO_2 and $SrTiO_3$) which require UV irradiation to excite them. Doping, dye-sensitization, and plasmon-induced charge separation have been mostly used to achieve visible-light-active photocatalysis. Nevertheless, abundant and nontoxic modified photocatalysts with high efficiency and stability are desirable. Here, I utilized a novel mechanism called interfacial charge transfer (IFCT). Two distinct charge transfer pathways: band-to-oxidant charge transfer (BOCT) and reductant-to-band charge transfer (RBCT) have been reported. The former has been well-studied, and high efficiency and stability in photocatalytic organic decomposition have been achieved over Cu(II)/TiO_2 system. However, the study on RBCT is scarce; thus, further investigations are required. Also, an exploration of other photocatalytic reactions via BOCT and RBCT is necessary. In other words, research on IFCT is partial as shown in Table 1; therefore, I want to build a comprehensive basis for IFCT via mechanistic and photocatalytic fuel production studies.

Table 1. Current situation on the IFCT study. The table shows what studies have been done previously (black characters) and what have not been done (red characters) on BOCT and RBCT pathway.



	Interfacial charge transfer (IFCT)	
	Band-to-oxidant (BOCT)	Reductant-to-band (RBCT)
Material	Cu(II)/TiO_2, Cu(II)/$SrTiO_3$, Cu(II)/ZnO, Fe(III)/TiO_2, Fe(III)/$BiVO_4$, Fe(III)/Bi_2O_3	Cr(III)/TiO_2, other semiconductors
Mechanism	Electron spin resonance (ESR), thin-film and photodeposition, more evidence is desirable	No evidence
Reaction	Organic decompositions (downhill reaction), fuel production (uphill reaction)	Organic decomposition (downhill reaction), but detailed study is needed; fuel production (uphill reaction)

Chapter 2. Understanding IFCT using a well-defined ultrathin film system and Kelvin probe force microscopy (KPFM)



Cr$_2$O$_3$/SrTiO$_3$ thin film system

Figure 1. KPFM observation of Cr$_2$O$_3$/SrTiO$_3$ on which visible-light was irradiated during the second-half scan. The downshift of surface potential difference (SPD) of Cr$_2$O$_3$ during the irradiation can be assigned to a direct electron excitation from Cr$_2$O$_3$ to SrTiO$_3$, leaving hole in Cr$_2$O$_3$.

Cr$_2$O$_3$/SrTiO$_3$ thin-film system was fabricated by depositing Cr$_2$O$_3$ ultrathin-film onto a single crystal SrTiO$_3$ substrate using a pulsed laser deposition (PLD) technique. The surface potential of Cr$_2$O$_3$ thin-film under dark and visible-light irradiation was investigated by a Kelvin probe force microscope (KPFM). A negative shift (Figure 1) of the Cr$_2$O$_3$ thin-film's SPD during the visible-light illumination can be assigned to an electron excitation from Cr$_2$O$_3$ to SrTiO$_3$, leaving holes in the thin film. On the other hand, CuO/SrTiO$_3$ showed a positive shift of SPD of CuO, indicating that electrons were excited from SrTiO$_3$ to CuO. Several thin film thicknesses were studied to reveal the optimum thickness. Considering the surface potential difference, 3 nm Cr$_2$O$_3$ showed the highest, whereas 90 nm Cr$_2$O$_3$ could not facilitate RBCT anymore. This result indicated that thinner Cr$_2$O$_3$ is necessary to facilitate RBCT. This chapter directly elucidated the interfacial charge transfer from Cr$_2$O$_3$ (SrTiO$_3$) to SrTiO$_3$ (CuO) using KPFM.

Chapter 3. Positioning the redox site on a patterned Cr$_2$O$_3$/SrTiO$_3$ ultrathin film system as a photocatalyst model

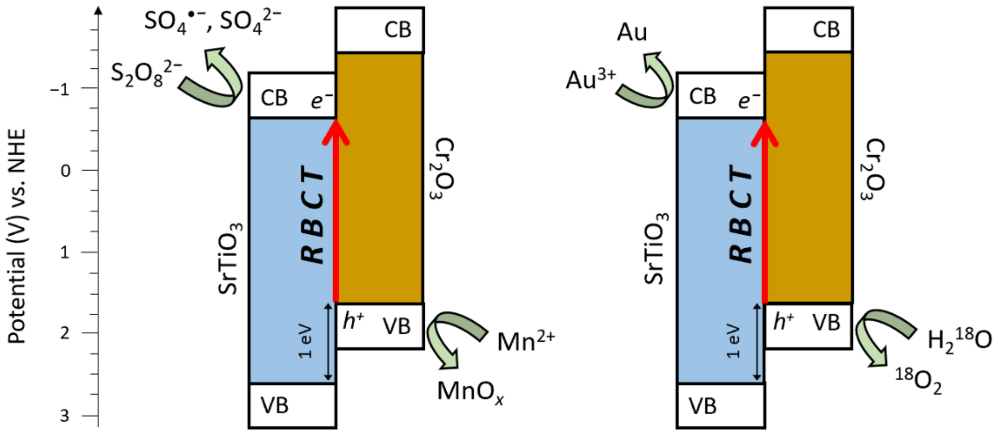


Figure 2. Schematic of the visible-light-driven one-step interfacial electron excitation, also referred to as RBCT, from the VB of Cr_2O_3 to the CB of $SrTiO_3$. (a) MnO_x photo-oxidation and (b) Au photo-reduction reactions in the Cr_2O_3/$SrTiO_3$ thin film system.

The reduction and oxidation sites in the Cr_2O_3/$SrTiO_3$ system were revealed by photodeposition method. Using an atomic force microscope, I observed that MnO_x was deposited on the thin film perimeter, indicating that holes were transferred onto Cr_2O_3. Meanwhile, Au was deposited on $SrTiO_3$, suggesting that electrons were excited to $SrTiO_3$. I also demonstrated that RBCT was able to drive oxygen evolution. By observing both photodeposition sites, lateral transport distances of electron and hole were estimated to be several tens nanometers from the thin film edge. In addition, by considering the occupied and unoccupied orbitals, RBCT can be explained by an one-step excitation from the valence band of Cr_2O_3 to the conduction band of $SrTiO_3$ (Figure 2). The horizontal (within 90 nm, Chapter 2) and lateral (several tens nanometers) charge transport distance suggested me to fabricate a Cr_2O_3/$SrTiO_3$ nanostructure in the next chapter.

Chapter 4. Photocatalytic environmental purification via RBCT under visible-light irradiation

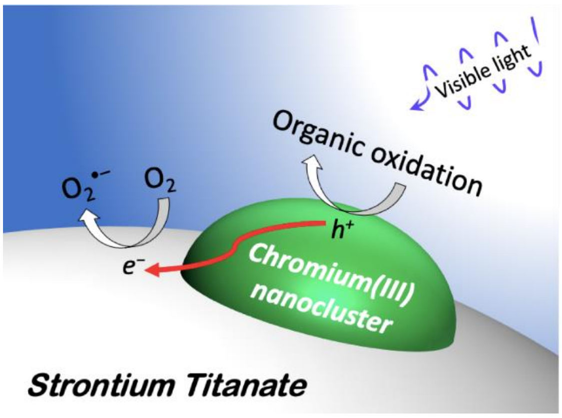


Figure 3. RBCT in Cr(III) nanoclusters-loaded $SrTiO_3$ powder system can initiate photocatalytic organic decomposition under visible-light irradiation.

According to the previous suggestion, Cr(III) nanoclusters with a size of a few nanometers were loaded onto the surface of $SrTiO_3$ powder by a facile impregnation method. Photocatalytic 2-propanol decomposition was successfully demonstrated over Cr(III) nanoclusters-loaded $SrTiO_3$ powder under visible-light irradiation. The action spectrum indicates that the apparent quantum yield (AQY) was 0.8% at 430 nm, and RBCT is indispensable to drive the reaction. To study the mechanism, *Operando* electron spin resonance (ESR) and photo/electrochemical study were conducted. ESR revealed that the initial electrons transfer from Cr(III) nanoclusters to the conduction band of $SrTiO_3$ took place. Consequently, the generated Cr(IV) decomposed gaseous 2-propanol into CO_2, and returned to Cr(III). Photo/electrochemical study suggested that Cr(III) nanoclusters facilitated the visible-light absorption while serving as the catalytic site for 2-propanol decomposition. Overall reaction is shown in Figure 3.

Chapter 5. Cathodic photoresponse and photoelectrochemical hydrogen evolution via BOCT under visible-light irradiation

I studied BOCT in Cu(II) nanoclusters-loaded TiO_2 in a three-electrodes configuration photoelectrochemical system. By applying a negative bias potential to the Cu(II)/TiO_2 photoelectrode, a cathodic photoresponse was observed surprisingly. In this system, electrons were excited from the valence band of TiO_2 to Cu(II) nanoclusters to drive hydrogen evolution. Meanwhile, holes went to the anodic side to drive oxygen evolution. Faradic efficiency was calculated to be 10.4% due to the reaction competition with Cu(II) reduction to Cu(0). This is the first demonstration of BOCT-driven photoelectrochemical water splitting without any sacrificial agent. A highly efficient photoelectrochemical water splitting via BOCT using Cu(II)/TiO_2/FTO could be achieved if the oxidation state Cu(II) nanoclusters can be preserved.

Chapter 6. Philosophical contributions

I explained the philosophical contribution of my thesis. That is, my work is the first effort to establish a comprehensive understanding of IFCT. In addition, the new finding on the photoelectrochemical water splitting driven by IFCT opens up a new window for future research direction. Last but not least, the combination of light irradiation-enabled KPFM and a well-defined thin film system will aid the understanding of interfacial charge transfer in various heterostructure systems. The abundance of materials and facile preparation method will give an insight into the engineering and industrial side. Strategies for future IFCT are finally proposed.

Chapter 7. Summary

This chapter summarizes the thesis.