

Electron Separation and Relaxation Dynamics in Anatase-Rutile Coupled Photocatalysts: Dependence on Excitation Wavelength and Rutile Particle Size

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Titanium dioxide (TiO_2) is a typical and important photocatalyst that has been widely used in many photocatalytic reactions. Anatase and rutile are two major crystal phases of TiO_2 . For many photocatalytic reactions, anatase shows much higher activity than rutile. More interesting is a phenomenon observed by many groups that the anatase-rutile coupled TiO_2 photocatalysts usually show higher photocatalytic performance than either pure anatase or pure rutile. Spatial separation of charge carriers by electron transfer between anatase and rutile has been considered as the main reason to explain the synergistic effect of anatase and rutile, but the detailed mechanism of the interphasial electron transfer is still unclear and on debate.

In our previous work^[1], femtosecond time-resolved near-IR spectroscopy has been used to investigate the interphasial electron transfer in anatase-rutile coupled TiO_2 photocatalysts. After the excitation at 370 nm with a fs pulse, a broad absorption corresponding to the free conduction band electrons appears in pure anatase (particle size ~ 30 nm). These conduction band electrons show a fast trapping process and a slow decay component in a sub-picosecond time scale. The time-resolved spectra of a pure rutile (particle size ~ 100 nm) catalyst show strong negative absorption at wavelength shorter than 1330 nm and weak positive absorption at the longer wavelength range. The negative absorption is due to the stimulated emission and the positive absorption is ascribed to the conduction band electrons. The reason for the weak absorption of the conduction band electrons in this rutile catalyst is explained by the low absorption efficiency of the electrons in TiO_2 with a large particle size. For anatase-rutile coupled catalyst, both of the positive and the negative absorption appears. Because the positive absorption from the electrons observed on rutile is weak, the strong positive absorption observed in this anatase-rutile coupled catalyst is mainly due to the electrons in the anatase part. The decay dynamics of these electrons in the anatase part shows only one slow decay component. The fast trapping process observed on pure anatase is not observed on this catalyst. These results indicate the presence of fast electron transfer from rutile to anatase within 100 fs.

To further understand the electron transfer mechanism, dependence of the electron separation and relaxation dynamics in anatase-rutile coupled photocatalysts on the wavelength of the excitation and the particle size of rutile component has been studied in this work. Figure 1 shows the time dependence of the absorption change of anatase powders excited by 370 nm, 355 nm, and 300 nm fs pump pulses. The density of the initially photogenerated electrons changes depending on the excitation wavelength. The electron relaxation dynamics is sensitive to the electron density in the anatase particles. When the electron density increases, the ratio of the fast decay component and the slow decay component decreases. Figure 2 shows the time dependence of the absorption of 4:1 anatase-rutile powders excited by 370 nm, 355 nm, and 300 nm fs pump pulses. All of these decay curves show only one slow decaying component. The result is different from pure anatase for

the excitation at 370 nm or 355 nm, but similar to for the excitation at 300 nm. These results indicate that the driving force for the electron transfer is probably the different electron density in anatase and rutile particles. When the photon energy of the pump pulse is close to the band gap of anatase, the density of the photogenerated electrons in anatase is low and the density of the photogenerated electrons in rutile particle is relatively high. Hence, many electrons in rutile diffuse into anatase particles quickly. When the 300 nm pump pulse is used to excite this anatase-rutile catalyst, the electron densities in both of anatase and rutile particles are high. Therefore, the electron transfer between anatase and rutile particles is not observed in an obvious way.

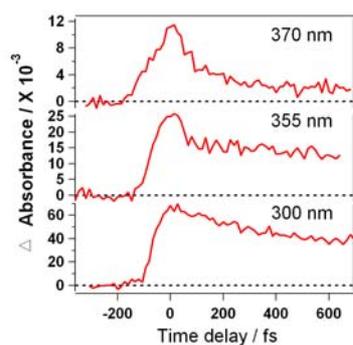


Figure 1 Time dependence of the absorption change of anatase powders excited by 370 nm, 355 nm, and 300 nm fs pump pulses.

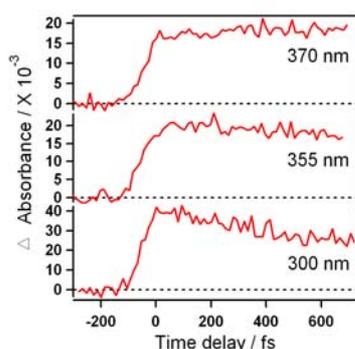


Figure 2 Time dependence of the absorption change of 4:1 anatase-rutile powders excited by 370 nm, 355 nm, and 300 nm fs pump pulses.

Sample	Apparent rate constant(min^{-1})
Anatase	0.22
Rutile (~100 nm)	0.09
4:1 Anatase-Rutile (R~100 nm)	0.27
10:1 Anatase-Rutile (R~100 nm)	0.30
Rutile (~15 nm)	0.04
4:1 Anatase-Rutile (R~15 nm)	0.24
10:1 Anatase-Rutile (R~15 nm)	0.32
Photolysis of MB	0.03

Table 1 Activities of TiO_2 photocatalysts on degradation of methylene blue.

To improve the electron transfer from rutile to anatase so as to increase the photocatalytic activity of anatase-rutile catalyst, one possible way is to decrease the distance for the electron transfer. It is expected that the efficiency of the electron transfer from rutile to anatase will increase with decreasing the particle size of rutile. To examine whether this anticipation is true or not, the same anatase was coupled with another rutile catalyst with a smaller particle size of ~ 15 nm. After the excitation at 370 nm with a fs pulse, a broad and strong absorption corresponding to the conduction band electrons appears in this rutile with the small particle size. These electrons do not decay in 800 fs. The 4:1 anatase-rutile (R~15 nm) coupled catalyst also gives a broad and strong absorption, and these electrons do not decay either in 800 fs. It is still difficult to judge whether the electron transfer efficiencies in anatase-rutile (R~100 nm) and anatase-rutile (R~15 nm) catalysts are similar or not. The studies on other anatase-rutile (R~15 nm) catalysts with different weight ratios of anatase and rutile are ongoing.

Table 1 compares the photocatalytic activities of different TiO_2 photocatalysts on degradation of methylene blue. Anatase shows a higher activity than rutile. The activities of anatase-rutile coupled catalysts are higher than anatase. The best synergetic effect is observed on 10:1 anatase-rutile (R~15 nm) catalyst. Though the activity of the small size rutile used in this study is low, 10:1 anatase-rutile (R~15 nm) catalyst shows the highest activity, which is possibly due to the high efficiency of the electron transfer from rutile to anatase in this catalyst.

Reference

[1] T. Chen and K. Iwata, The 90th annual meeting of the chemical society of Japan, 3D1-44, Higashi Osaka, (2010).