Dynamics of Photocarriers in Ga_2O_3-based Photocatalyst Studied by Transient Absorption Spectroscopy

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Ga_2O_3 is a wide bandgap material that is active for overall water splitting owing to its suitable band structures for H_2 and O_2 generation. By doping metal ions such as Zn^{2+} in Ga_2O_3, a remarkably high photocatalytic activity has been achieved with 71% quantum efficiency.[1] It is often believed that the introduction of dopants induces mid-gap states, which affect the optical absorption properties. Understanding the behavior of photogenerated electrons and holes is indispensable to determine the role of dopants in the enhancement of photocatalytic activity. Here, we investigated the dynamics of photocarriers in Ga_2O_3 and $ZnGa_2O_4$ powder photocatalysts. The effects of Ta and Nb doping on $ZnGa_2O_4$ were also examined. In order to study the dynamics of photocarriers, we performed transient absorption spectroscopy.[2-3]

In the experiments, each Ga_2O_3-based powder was excited by 266 nm laser pulses (0.04 mJ per pulse, 6-ns duration, 1 Hz).

We first examined the transient absorption spectra of Ga_2O_3 powder after 266 nm excitation. The spectra are shown in Figure 1A. We can observe two absorption features: negligible absorption at 9000 – 4000 cm^{-1} and discernable absorption < 4000 cm^{-1}, which is monotonically increasing towards lower wavenumber. The spectral shape of the absorption at < 4000 cm^{-1} is a characteristic of free electrons and/or shallowly trapped electrons.[2-3] In the case of $ZnGa_2O_4$ (Fig. 1B), the spectra also show strong absorption < 4000 cm^{-1}; however, the absorption at 9000 – 4000 cm^{-1} is clearly observable, which is absent in the absorption spectra of Ga_2O_3. Therefore, the absorption at 9000 – 4000 cm^{-1} can be attributed to absorption of trapped electrons at the defects induced by Zn incorporation in Ga_2O_3 producing $ZnGa_2O_4$.

The effect of Zn incorporation was further examined by observing the decay of free electrons probed at 2000 cm^{-1} (Fig. 2). The decay of free electrons is faster in $ZnGa_2O_4$ than in Ga_2O_3. This result suggests that the defects in $ZnGa_2O_4$ play a key role to trap the electrons. However, when Nb is doped in $ZnGa_2O_4$, the number of surviving free electrons drastically increases, suggesting that Nb dopant is effective to produce long-lived free electrons. The detailed results will be presented at the symposium.

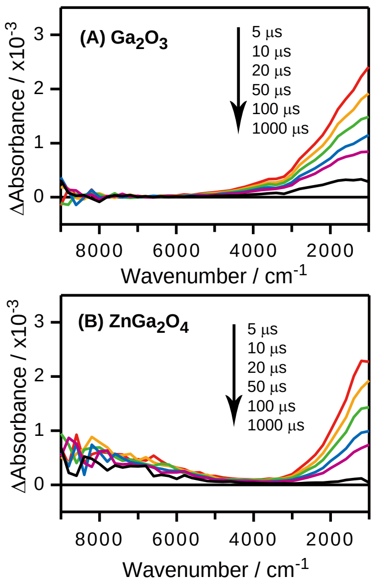

Fig.1 Transient absorption spectra of Ga_2O_3 (A) and $ZnGa_2O_4$ (B) powder photocatalysts.

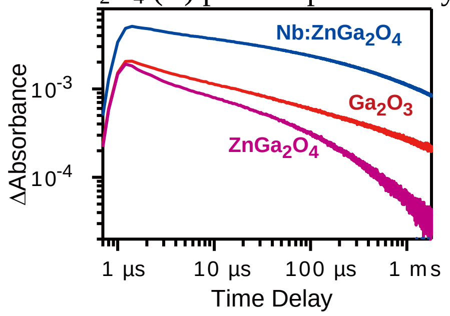

Fig. 2 Decay profiles of free electrons in Ga_2O_3, $ZnGa_2O_4$, and Nb-doped $ZnGa_2O_4$ probed at 2000 cm^{-1} in a vacuum.

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