

Investigation of photo-excited carrier dynamics in hematite and the effect of surface modifications by advanced transient grating technique

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Hematite has attracted great attention from many researchers because it can work as a photoanode for water splitting that has great potential for solar energy conversion. However, it has multiple limiting factors such as short electron-hole lifetime and poor hole transfer efficiency thus it is very difficult to get enough solar to hydrogen (STH) efficiency to be implemented. In order to overcome the problem, recently, one of our co-authors (Wang) and co-workers investigated hematite films coated with amorphous NiFeOx and found it showed a high photo-electrochemical (PEC) performance.^[1-3] In the present study, we investigated photo-excited dynamics of the hematite film coated with NiFeOx to get its kinetic information, which helps us further understand the effect of the coating on the PEC performance.

In order to study the carrier dynamics, we employed heterodyne transient grating (HD-TG) technique. Briefly, this technique is a time-resolved method in which the refractive index change induced by photo-chemical or physical processes is monitored and is sensitive to the dipole change at the solid/liquid interface.^[4] The sample, hematite film, was pumped by the irradiation of a UV light (355 nm) and the response was measured via the diffraction of the probe light (638 and 785 nm). The signal was detected by a photodiode and amplified by a voltage amplifier.

The HD-TG response of hematite film coated with NiFeOx was measured in acetonitrile (ACN), an inactive solvent, to get a reference response and presented as black line in Fig. 1. As can be seen in the response, it featured two different components after a quick rise, a fast decay part from 10^{-6} to 10^{-5} s and a slow decay part from 10^{-5} to 10^{-4} s. The time constants for each component, 3 μ s for the faster one, 0.1 ms for the slower one, were clearly extracted by the maximum entropy method (MEM) as shown in the inset of Fig. 1. We also succeeded to assign the rising part to trapping of electrons to the surface states and the following relaxations to the decay of electrons (faster) and holes (slower) by using a different probe light (785 nm) and a hole scavenger, ethanol.

In order to clarify the role of NiFeO_x coating on the carrier dynamics of hematite, HD-TG

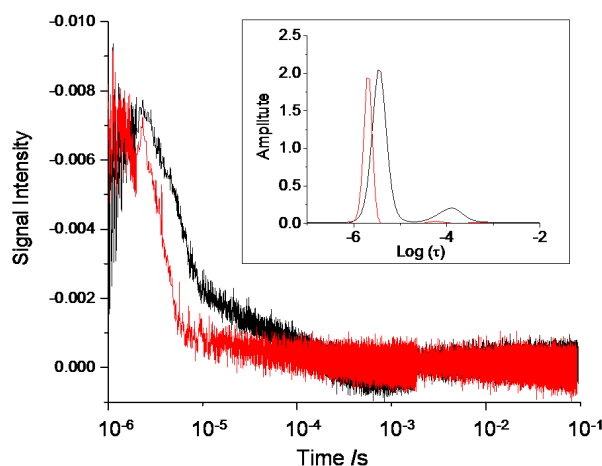


Figure 1. HD-TG response of hematite film coated with NiFeO_x (Black) and without the coating (Red) probed by 638 nm. The time constant distribution was analyzed by using MEM analyses in the range of $\sim 10^{-6}$ to 10^{-2} s.

response of bare hematite film was also measured (the red line in Fig. 1) and compared with the coated one. MEM analyses was also employed to get the time constants of the bare hematite. As can be seen in the inset of the figure, the sample with NiFeO_x showed two peaks at 3 μ s and 0.1 ms, while the sample without NiFeO_x showed two peaks at 2 μ s and 0.05 ms. The increase in the intensity of the slower component indicates that the number of the trapped holes increased for the NiFeO_x coating, while it did not affect the number of the trapped electrons. Therefore, it was demonstrated that the amorphous NiFeO_x coating on a hematite film plays a role to increase the number of the trapped holes at the surface because the surface recombination was retarded.

In the conference, we will also discuss the charge carrier dynamics of hematite film in water, which is much closely related with the efficiency of the oxygen generation reaction.

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