# The electron transfer channel in the sugar recognition system assembled on gold nano particles

T. Goto,[*1] T. Hashimoto,[*1] D. P. Sari,[*2] and I. Watanabe[*3]

The recently reported electrochemical sugar recognition system consisting of a gold nano particle (GNP) with a diameter of 12 nm, a ruthenium complex and a phenylboronic acids, attracts much interest because of its high sensitivity for various sugars such as D-glucose or D-fructose. When sugar molecules are "recognized" by the phenylboronic site, the response of electrochemical voltammetry of the ruthenium complex site drastically changes, enabling the system to work as a highly sensitive sugar-sensor.[1,2] In this recognition process, the change in the electronic state at the phenylboronic acids site caused by sugar must be transferred to the ruthenium complex site. The purpose of this study is to find out by LF-$\mu$SR technique a channel of the electron transfer from the phenylboronic acid site to the ruthenium complex via gold nano particle. By its finding, we will be given a better understanding of the sugar-recognition mechanism, and also, a possibility to develop a sensor with still higher sensitivity and more functions.

As the present system includes alkyl-chains in the ruthenium complex and the phenylboronic acid site, the injected muons pick up one electron to form a neutral atomic state, which is soon thermalized and bonded to a relatively-reactive site on the chain. The brought-in electrons may show one-dimensional motion along the chain, if the electron transfer channel between the ruthenium complex and the phenylboronic site exists.

This behavior can be detected sensitively by measuring the muon-spin relaxation process, which is caused by the magnetic interaction between the muon spin and the moving electron produced by muon itself. In other words, in place of the attachment of sugar molecules to phenylboronic acid site, one utilizes muon as a trigger to induce a moving electron and also as an observer of it. This method is known as the muon-labelling measurement.

The characteristic dimensionality of the electron motion can be readily studied by measuring LF dependence of $\mu$SR relaxation rate $\lambda$;[3] for one-dimensional motion, $\lambda$ is expected to be proportional to $(H_{\rm LF})^{-1/2}$, where $H_{\rm LF}$ is the externally applied field along the muon spin polarization. This method was first applied to the polaron motion in oganic polymer chains,[4] and also successfully to the typical one dimensional system, DNA.[5]

Zero (ZF) and longitudinal (LF) field-$\mu$SR measurements at room temperature were performed on a powder sample at RIKEN-RAL Muon Facility using a spin-polarized pulsed surface-muon ($\mu^+$) beam with a momentum of 27 MeV/$c$. The muon spin depolarization

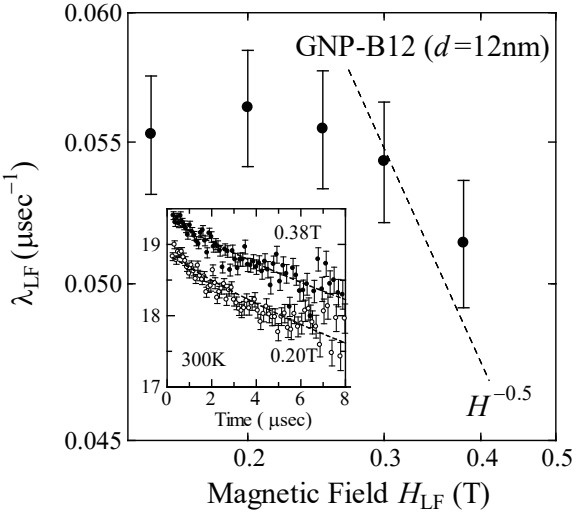


Fig. 1. Temperature dependence of dynamical component of relaxation rate $\lambda$ under various longitudinal fields $H_{\rm LF}$. The inset shows the typical depolarization curves of the asymmetry (%) with fitted functions. Each curve is vertically shifted for clarity.

data above 0.1 T were analyzed with the function $e^{\lambda\tau}$, where $\lambda$ is the depolarization rate due to the dynamical spin fluctuation. Note that in this field region, the effect of quasi static nuclear spins or $G_{\rm KT}$, Kubo-Toyabe function is neglected.

The field dependence of $\lambda$ is shown in Fig. 1. With decreasing $H_{\rm LF}$ from the highest field 0.38 T, $\lambda$ showed a slight but finite increase until $H_{\rm LF} \cong 0.2$ T, below which $\lambda$ saturates. An appreciably high depolarization in the totally non-magnetic compound indicates that some muon-triggered moving electron process exists. The observed increase is weaker than expected for the one dimensional diffusion case. This indicates that the contribution from the diffusion process has the lower boundary in the fluctuation spectrum, as is evident from the functional form of $\lambda H_{\rm LF}$ dependence, and in fact is reported for previous report.[4]

In order to confirm that the observed behavior of $\lambda$ comes from the one-dimensional movement along alkyl-chain, investigation on wider field region or equivalently on wider fluctuation spectrum, including NMR is inevitable, and is now on the progress.

*1 Faculty of Technology and Science, Sophia University
*2 SIT Research Laboratories, Shibaura Institute of Technology
*3 RIKEN Nishina Center

References

1) A. Endo *et al.*, Anal. Methods **6**, 8874 (2014).
2) T. Goto *et al.*, IEEE Trans. Mag. **55**, 2300404 (2019).
3) Risch and Kehr, Phys. Rev. B **46**, 5246 (1992).
4) F. Pratt *et al.*, Phys. Rev. Lett. **79**, 2855 (1997).
5) E. Torikai *et al.*, Hyperfine. Int. **138**, 509 (2001).