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Long range Charge transport through bio-engineered E2 ferritin based molecular junctions

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Abstract

The study of charge transport (CT) in (bio)molecular tunnel junctions (MTJs) as a function of molecular length and temperature paves the way for understanding the mechanism that enables long-range CT for many biological functions such as DNA transcription, enzymatic catalysis, photosynthesis etc. [1-3]. However, there exists no consensus about the general mechanism of CT. Herein we report a detailed study of CT through bio-engineered E2 ferritin based MTJs. We observed weakly temperature and length dependent CT suggesting that the long-range CT is dominated by sequential tunnelling in E2 ferritin MTJs. We also observed a reversible switching of shape and current density for 3000 Fe loaded E2 ferritin based MTJs and detailed study will be presented.

1. Introduction

The mechanism of CT has been investigated in biological systems such as Photosystem-I (7 nm), halorhodopsin (6 nm), azurin (3.5 nm) bacteriorhodopsin (5 nm) etc. based MTJs and mechanisms of CT have been proposed as direct tunnelling [4-6] and hopping [7]. However, there is no consensus to towards a general CT mechanism or mechanisms of CT that are system specific. Investigation of CT as a function of molecular length and temperature allows us to establish the mechanisms such as hopping transport, direct tunnelling or the intermediate sequential tunnelling regime.

The measured current density (J) across the tunnel junction as a function of molecular length (d) is fit into the general tunnelling equation to obtain the value of the tunnelling decay coefficient (β):

$$J = J_0 exp^{(-\beta d)} \quad , \qquad (1)$$

where J_0 is the current density when $d=0$. Temperature dependent J(V) measurements are used to calculate the activation energies with the Arrhenius equation,

$$J = J_0 exp^{(-E_a/k_B T)} \quad , \qquad (2)$$

where k_B is the Boltzmann constant and T is absolute temperature (in K). Direct tunnelling is length dependent and independent of temperature (β> 2 nm^{-1}, E_a~0). Hopping transport is temperature dependent and independent of length (β~0, E_a ~ hundreds of meV). An intermediate sequential tunnelling regime is characterised by a weak temperature and length dependence (β <2 nm-1, E_a ~ tens of meV) [8, 9].

A key reason why a consensus in CT mechanism studies is missing is due to a lack of systematic studies of CT as a function of both, length and temperature. Reports of CT across bio-MTJs are either lacking length dependent [4-6] or temperature dependent [10-12] CT characterisation which do not capture the entire picture. Recently, a detailed investigation of CT was reported for ferritin based MTJs as a function of both length and temperature up to 12 nm with a transition from direct to sequential tunnelling at 7 nm length [8]. Here, we investigate CT in bio-engineered E2 ferritin protein systematically as a function of length (from 13.3 nm to 24.6 nm) and temperature.

2. Results and discussion

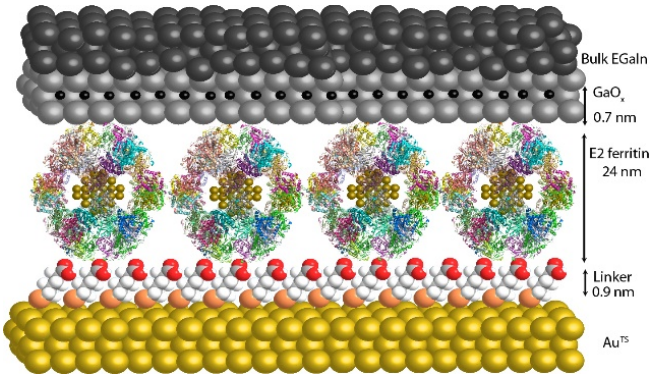

Fig. 1 Schematic of Au^{TS}-S-C_6-E2 ferritin//GaO_x/EGaIn MTJ

We report a detailed study of CT as a function of length and temperature in E2 ferritin (~25 nm) based MTJs with non-destructive liquid metal alloy eutectic Gallium-Indium (EGaIn) as the top electrode. The Fe loaded E2 ferritin was obtained from bio-engineered E2 protein (isolated from *Geobacillus stearothermophilus*) with Fe binding frog M-ferritin-

mimicking peptides [13]. We formed MTJs with self-assembled E2 ferritin on template stripped (TS) Au substrates (Fig. 1). We used TS bottom electrodes as they have been shown to be smoother and defect-free, as compared to as-deposited metal substrates, and allow characterisation of the SAM rather than substrate defects [14, 15]. For length-dependent CT studies, we modulated the width of the bio-molecular tunnelling barrier (d) as a function of the Fe loading (1000 Fe (13.3 nm) to 3000 Fe (24.6 nm)) in the E2 ferritin core. We investigated CT as a function of temperature in E2 ferritin based MTJs in the 150-340 K range. We observed weakly temperature dependent CT ($E_a \leq 50$ meV) and a tunnelling decay coefficient $\beta = 0.17 \pm 0.01$ nm^{-1} which is smaller than previously reported [4, 7, 16]. Based on these observations, we suggest a sequential tunnelling mechanism CT in our E2 ferritin MTJs.

For temperature dependent CT studies for T <240 K, we observe a change in current density and shape of the $J(V)$ curve in the temperature range 220-230 K for E2 ferritin based MTJs. We observe a reversible transition in the junction with 3000 Fe E2 ferritin whereas an irreversible transition is observed in lower Fe loaded 2000 Fe E2 ferritin. From these results, we suggest that the observed reversible transition may be due to following: (i) spin-crossover phenomena as in the case of $[Fe(H_2B(pz)_2)_2(C_{12}\text{-bpy})]$ complex nano-structures that pass from high spin state to low spin upon cooling from 300 K to 100 K or (ii) a temperature dependent phase transition [17]. Temperature dependent X-ray magnetic circular dichroism (XMCD) and superconducting quantum interference device (SQUID) were measured to ascertain the spin crossover phenomenon. To understand the change in the shape and current density of the $J(V)$ curve due to the phase transition phenomenon, we carried out differential scale calorimetry (DSC) measurements for powder samples of the E2 ferritin. The results of these detailed studies will be presented in the conference. This observation opens applications for E2-ferritin based MTJs as memory devices.

3. Conclusions

We conclude that CT in the E2 ferritin based MTJs occurs by sequential tunnelling and our investigation improves the understanding of long-range CT in biological systems. We observed reversible and irreversible switching behaviour in the E2 ferritin based MTJs and are currently investigating the phenomenon responsible for our observations.

We further propose that study of tunnelling magnetoresistance (TMR) for memory device applications can be done with E2 ferritin based MTJs.

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References

[1]. [1] M. A. Grodick, N. B. Muren, J. K. Barton, Biochemistry **54**, (2015) 962–973.

[2]. S. Y. Reece, J. M. Hodgkiss, J. Stubbe, D. G. Nocera, Philos. Trans. R. Soc. B Biol. Sci. **361**, (2006) 1351–1364.

[3]. M. R. Wasielewski, J. Org. Chem. **71**, (2006) 5051–5066.

[4]. O. E. Castañeda Ocampo, P. Gordiichuk, S. Catarci, D. A. Gautier, A. Herrmann, R. C. Chiechi, J. Am. Chem. Soc. **137**, (2015) 8419–8427.

[5]. S. Mukhopadhyay, S. Dutta, I. Pecht, M. Sheves, D. Cahen, J. Am. Chem. Soc. **137**, (2015) 11226–11229.

[6]. L. Sepunaru, I. Pecht, M. Sheves, D. Cahen, J. Am. Chem. Soc. **133**, (2011) 2421–2423.

[7]. L. Sepunaru, N. Friedman, I. Pecht, M. Sheves, D. Cahen, J. Am. Chem. Soc. **134**, (2012) 4169–4176.

[8]. K. S. Kumar, R. R. Pasula, S. Lim, C. A. Nijhuis, Adv. Mater. **28**, (2016) 1824–1830.

[9]. N. Amdursky, D. Marchak, L. Sepunaru, I. Pecht, M. Sheves, D. Cahen, Adv. Mater. **26**, (2014) 7142–7161.

[10]. M. Baghbanzadeh, C. M. Bowers, D. Rappoport, T. Zaba, M. Gonidec, M. H. Al-Sayah, P. Cyganik, A. Aspuru-Guzik, G. M. Whitesides, Angew. Chemie - Int. Ed. **54**, (2015) 14743–14747.

[11]. G. I. Livshits, A. Stern, D. Rotem, N. Borovok, G. Eidelshtein, A. Migliore, E. Penzo, S. J. Wind, R. Di Felice, S. S. Skourtis, et al., Nat. Nanotechnol. **9**, (2014) 1040–1046.

[12]. L. Xiang, J. L. Palma, C. Bruot, V. Mujica, M. A. Ratner, N. Tao, Nat. Chem. **7**, (2015) 221–226.

[13]. T. Peng, D. Paramelle, B. Sana, C. F. Lee, S. Lim, Small **10**, (2014) 3131–3138.

[14]. L. Yuan, L. Jiang, D. Thompson, C. A. Nijhuis, J. Am. Chem. Soc. **136**, (2014) 6554–6557.

[15]. L. Yuan, L. Jiang, B. Zhang, C. A. Nijhuis, Angew. Chemie - Int. Ed. **53**, (2014) 3377–3381.

[16]. H. Yan, A. Johan, R. L. McCreery, M. Luisa, D. Rocca, P. Martin, P. Lafarge, J. Christophe, Proc. Natl. Acac. Sci. **110**, (2013) 5326–5330.

[17]. K. S. Kumar, M. Studniarek, B. Heinrich, J. Arabski, G. Schmerber, M. Bowen, S. Boukari, E. Beaurepaire, J. Dreiser, M. Ruben, Adv. Mater. **30**, (2018) 1–7.