Highly controllable molecular rectifier realized by interfacial design in molecular heterojunction with two-dimensional materials

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Abstract

Since Aviram and Ratner initially proposed the possibility of a molecular-scale rectifier in 1974, diverse type of molecular diodes driven by a specific molecular itself or the asymmetric coupling has been extensively demonstrated. Here, we suggest a simple approach toward highly controllable molecular-scale rectifier using a molecular heterojunction formed by either a simple alkanethiol or oligophenylene thiol molecular basis with two-dimensional semiconductors (MoS₂ and WSe₂). Depending on the number of MoS₂ layers, molecular length, and molecular species, the rectifying features can be highly controllable. A more-comprehensive understanding of these rectifying features was thoroughly investigated based on multi-barrier tunneling model and metalinsulator-semiconductor current expression based on simple tunneling picture according to voltage polarities.

1. Introduction

Since the inception of the conceptual molecular rectifier consisting of a donor and acceptor separated with σ -bridge that was initially envisioned by Aviram and Ratner, a wide range of molecular diodes has been proposed and investigated [1-3]. Recently, Chen et al. demonstrated that the 'supramolecular diode' with rectification ratio (*RR*) > 10⁵ in EGaIn/SC₁₅Fc-C=C-Fc/Pt molecular junction system, which is the result based on an increase in the number of conducting molecules in only one direction of bias driven by electrostatic interactions between the top electrode and charged terminal groups of the SAMs [2].

Here, we propose a new class of molecular rectifier realized by molecular heterojunction stacked of the Au/the 2D semiconductors (MoS₂ or WSe₂)/standard self-assembled monolayer (SAMs) (alkyl- or oligophenylene monothiol)/Au probe tip using conductive atomic force microscopy (CAFM) technique. Our new class of molecular rectifier with $RR > 10^3$ was observed and can be controllable according to the number of MoS₂ layers, the type of 2D semiconductors, the molecular length, and the molecular group. Also, a comparison of the experimental RR and theoretical RR that is based on Simmons model and metal-insulator-semiconductor current expression based on simple tunneling picture was made, and it is confirmed that both are in sound agreement.

2. Results and Discussions

Figure 1a shows a schematic diagram of a molecular heterojunction structure composed of a self-assembled monolayers (SAMs) of molecules and 1_L-MoS₂ stacked on the Au/SiO2/Si substrate, whose electrical properties are investigated by conductive atomic force microscopy (CAFM) technique. Five standard molecular species that are distinguished according to the molecular length and the HOMO-LUMO gap (i.e., benzene-1-monothiol (denoted as OPT1), biphenyl 4-monothiol (OPT2), 1-octanemonothiol (C8), 1-decanemonothiol (C10), and 1-dodecanemonothiol (C12)) are used. As a representative two-dimensional (2D) semiconductor, an ntype $N_{\rm L}$ -MoS₂ with different number of the layers ($N_{\rm L} = 1_{\rm L}$, 2_L , and 3_L) and p-type 1_L -WSe₂ are used to form a heterojunction with SAMs in this study (right of Fig. 1a). Introducing 2D semiconducting material (sub-1 nm) at the molecule/Au interface allows us to modify the interfacial band profile across the junction while maintaining the molecular-scale junction size. In addition, the appropriate choice of 2D semiconductor types (n- or p-type) and its number of the layers enables the adjustment of the interfacial barrier between SAMs and 2D semiconductors in addition to the majority carriers in a highly designed manner. Figure 1b shows the optical images and topological line profiles of 1_L-MoS₂ and 1_L-WSe₂ exfoliated on the SiO₂/Si substrate. The measured height of ~0.7 nm indicates that both MoS₂ and WSe₂ are monolayer. In the Raman spectra shown in Fig. 1c, the E^{1}_{2g} and A_{1g} vibrational modes were observed at 383 cm⁻¹ and 402 cm⁻¹ with spacing $\Delta = 18.5$ cm⁻¹ for 1_L-MoS₂ (red line) and at 247 cm⁻¹ with spectral overlapping for 1_L-WSe₂ (blue line), confirming their monolayer structures.

Figure 1d shows the representative *I-V* characteristics for five different molecular junctions such as Au/OPT2/1_L-MoS₂/Au (red solid circle), Au/OPT2/1_L-WSe₂/Au (cyan solid circle), Au/OPT2/Au, Au/WSe₂/Au, and Au/MoS₂/Au. Among them, in the cases of junctions composed of only TMDs or OPT2 (presented by dashed lines), all *I-V* characteristics exhibit symmetric behaviors ($RR = \sim 1$, defining as |*I* (V = 1 V)|/|*I* (V = -1 V)|) due to the single transport barrier located in between the Fermi level (E_F) of Au electrodes. However, when the molecular heterojunctions are formed with 1_L-MoS₂ and 1_L-WSe₂, the *I-V* curves are asymmetrically changed. In particular, their *RR* values are strongly depending on the 2D semiconductor types. The OPT2/1_L-MoS₂ junction exhibits $RR = 1.79 \times 10^3$ that is much larger than that of OPT2/1_L-WSe₂ junction (RR = 2.31) (Fig. 1d). Also, this



Fig. 1 a. (left) Schematic of a molecular junction composed of Au/OPT2/MoS₂ stacked on an Au/SiO₂/Si substrate under $F_L = 1$ nN of the Au tip using CAFM technique. (right) The molecular structures for (i) oligophenylene-based monothiol (OPT1 and OPT2) and (ii) alkyl-based monothiol (C8, C10, and C12) are shown. **b.** Topological line profiles of 1_L-MoS₂ (left) and 1_L-WSe₂ (right) at the position of black arrow in the optical microscope image (inset), respectively. **c.** Raman spectra for the exfoliated 1_L-MoS₂ (red line) and 1_L-WSe₂ (blue line). **d.** Representative *I-V* characteristics for five different molecular junctions such as Au/OPT2/1_L-MoS₂/Au (red solid circle), Au/OPT2/1_L-WSe₂/Au, and Au/MoS₂/Au (dotted line). **e.** Contour current plots of our heterojunction for OPT2/1_L-MoS₂ (left) and OPT2/1_L-MoS₂ (right), respectively. **f.** Statistical histogram of *RR* for OPT2/1_L-MoS₂ junction (red) and OPT2/1_L-WSe₂ junction (cyan), respectively.

value exceeds beyond the theoretical rectification limit (RR = 20) of a molecular junction functionalized with any alkylbased or conjugated SAMs. More specifically, the OPT2/1_L-MoS₂ junction has a distinct asymmetry compared with the OPT2/1_L-WSe₂ junction, exhibiting the lower *I* at *V* < 0 and the higher *I* at *V* > 0. Such rectifying behaviors were reproducibly obtained for both molecular heterojunctions when we statistically investigated the *I*-*V* characteristics at different positions (at least 20 and 100 times, respectively), as shown in the contour plots in Fig. 1e. The statistical histogram of *RR* for OPT2/1_L-MoS₂ junction is found to be a higher value (*RR* = $1.68 \pm 0.63 \times 10^3$) than that for OPT2/1_L-WeS₂ junction (*RR* = 2.36 ± 0.77) (Fig. 1f). The details of charge transport mechanism according to voltage polarities are discussed in presentation.

3. Conclusions

In this study, we first implement a controllable molecular rectifier realized by molecule-2D semiconductor heterojunction structure (< 2 nm) and found that the RR was > 10³ that

is one of the highest ratio in molecular junction. The rectifying feature is mainly originated from different transport pathway depending on voltage polarities. Our suggested heterojunction structure has the potential to improve the *RR* by using various 2D semiconductor and molecular SAMs.

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