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ABSTRACT

As a basic electronic component, the diode has drawn much attention in single-molecule electronics. However, the single-molecule diode is limited to the conventional diode mode, switching to "on" with a forward voltage and to "off" whenever an opposite voltage is applied. We report on a paradigm for designing a single-molecule tidal diode, which enables gate-controlled reversible rectifying behavior. In the Au₂₅-R single-molecule transistors constructed by us, we observed clear rectification and achieved an electrically controllable reversible diode effect. The backward rectification ratio reached the maximum value of 30 at a negative bias voltage of -30 mV, while the forward rectification ratio was slightly smaller. We used an asymmetrical coupling model and a Landauer resonant tunneling model to explain the reversible diode effect and its dependence on temperature. The integration of bidirectional tunable diodes in a single-molecule device creates an avenue of research and allows the discovery of a set of traffic rules for the electronic world in the future.

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To improve device performance and to cope with the quantum effects associated with device miniaturization, single molecules are considered as potential device building blocks.^{1–4} Singlemolecule electronics (SMEs) are currently studied for the integration of molecules into electronic devices, including switches, diodes, transistors, sensors, etc.^{5–13} Conventional diodes are basic electronic components that allow currents to flow in one direction only. Extensive studies have been carried out on molecular diodes over the last few decades,^{14–19} such as the discussion on the rectification mechanism,¹⁵ attempts at high-frequency operation,¹⁷ and improvements to rectification performance.^{16,18} Great progress has been shown in the realization of molecular diodes with enhanced rectification ratios (RRs) exceeding 10^{5} .¹⁸

As their name suggests, single-molecule diodes consist of a single molecule, which offers the advantage of lower power density and less energy dissipation.²⁰⁻³⁰ They have been used in junctions featuring asymmetric molecular rods,^{20,22-24,28-30} asymmetric tunneling barriers,^{21,27} asymmetric molecule–electrode linkers,²⁵ asymmetric electrode environments,²⁶ etc., as well as showing enhanced RRs exceeding 100;^{26,28} inversion of the rectification occurs as the molecule is transferred mechanically from the substrate to the tip.²⁷ However, it is not possible to control the direction and magnitude of the rectification simultaneously, and their operating voltages generally exceed a few hundred millivolts, which limit the scope of their application.

We report on a tidal diode based on metal clusters with a variety of ligands. There has been considerable interest in nanoclusters composed of no more than a few hundred atoms as the functional part of electronic devices due to their size- and structure-dependent physical properties.^{31–34} We demonstrate single-molecule diodes comprising Au₂₅-R clusters sandwiched between gold electrodes, which exhibit a maximum RR of about 30 and for which the direction of rectification can be tuned efficiently and predictably by the gate voltage. The Au₂₅-R clusters' core has different elements, such as S, P, and Cl, and the electrodes are more easily attached to these atoms to form asymmetric couplings during electromigration as the peripheral atoms are not as stable as those in the vicinity of the cluster core. We use a Landauer resonant tunneling model with a strong asymmetric coupling to explain the reversible diode effect and its dependence on temperature.

The rod-like structure of $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$ (Au₂₅-R) was obtained by means of a chemical reaction.³⁵ In order to determine the nature and structure of Au₂₅-R, UV–vis absorption spectroscopy was carried out, and the target obtained was confirmed to have a rod structure. Its crystal structure was also measured in detail using a single crystal x-ray diffraction method; the HAADF-STEM image also indicated a rod-like structure. Further details are given in the supplementary material (S1 and S2).

Details of the device fabrication procedure are consistent with those described in Refs. 31 and 33. The single-molecule transistors (SMTs) were constructed using a feedback-controlled electromigration break junction (FCEBJ) method after the solution of Au₂₅-R was dropped onto the prepared device chips. The transport characteristics were then investigated at cryogenic temperatures using Keithley 6430/2450 source meters.

The rectifier molecule proposed by us has a rod-shaped cluster of Au₂₅-R [inset of Fig. 1(a)]. The UV-visible absorption spectrum [Fig. 1(a)] shows a distinct peak at 677 nm and several additional peaks at shorter wavelengths. The absorption peak at 677 nm is attributed to an electronic transition of the dimeric structure, while the absorption peaks seen in shorter wavelength regions (<500 nm) are assigned to electronic transitions in each Au₁₃ unit.^{36–39} Figure 1(b) demonstrates the current (I_{ds}) traces as a function of the applied bias voltage (V_{ds}) during a typical FCE procedure. The inset in Fig. 1(b) shows a schematic diagram of the device measurement. The I_{ds} - V_{ds} curves [Fig. 1(c)] show distinct nonlinear behavior and a tunable Coulomb blockade region, which indicates that the molecular energy levels are modulated by gate voltages (Vg). In addition, the current under negative bias voltage is significantly larger than the current under positive bias, showing a clear diode effect. Figure 1(d) shows a Coulomb oscillation pattern an oscillation pattern at a small bias voltage of 2 mV, with more than two obvious peaks located at gate voltages of about ~8 and ~18 V. These peaks correspond to cases where the chemical potential of the molecule is lifted close to the Fermi level of the source and drain electrodes, allowing an electron to tunnel resonantly through the molecule.

To investigate the diode effect, the current data are treated using absolute values. Figure 2(a) shows two *I*–*V* curves measured on different sides of a charge degeneracy point ($V_g = \sim 8 \text{ V}$), which clearly demonstrates the reversal of the direction of rectification. The RR is defined as RR(V_{ds}) = $|I(-V_{ds})/I(V_{ds})|$ when $V_{ds} < 0$, while RR(V_{ds}) = $|I(V_{ds})/I(-V_{ds})|$ when $V_{ds} > 0$. We show the RR– V_g curves at five different bias voltages in Fig. 2(b). The backward RR



FIG. 1. (a) UV–vis spectra of Au₂₅-R nanorod clusters. Inset: Schematic image of Au₂₅-R nanorods. Color code: Cl–green; S–red; P–orange. (b) A typical FCE process (the inset shows the device structure). (c) Representative *I–V* curves measured at 1.6 K for different gate voltages. (d) Coulomb oscillation. The current ($V_{ds} = 2$ mV) was measured as a function of gate voltage, and the two dominant peaks for the positive gate voltage correspond to charge degeneracy points.



FIG. 2. (a) *I*–*V* curves at two different gate voltages; absolute values are taken for current in the figure for comparative purposes. (b) The RR– V_g curves at five different values of $V_{ds.}$ (c) Current stability diagram of the device. The current is coded by color as a function of gate voltage V_g and bias voltage $V_{ds.}$ (d) RR as a function of V_g and V_{ds} . The direction of rectification can be reversed by varying V_g .

 $(V_{\rm ds}<0)$ reaches a maximum value of 30 at a negative bias voltage of -30 mV, while the forward RR is slightly smaller.

Figure 2(c) shows a two-dimensional (2D) map of absolute source-drain current as a function of $V_{\rm ds}$ and $V_{\rm g}$. Areas in blue represent regions with low current, while areas in red show high current. There are two diamond-shaped resonant tunneling regions with clear slopes in the edges. The diamond shapes in this current intensity diagram are skewed due to the asymmetry of the coupling. We then produced a 2D map of RR as a function of $V_{\rm ds}$ and $V_{\rm g}$ in Fig. 2(d). For regions from $V_{\rm g} = 0-10$ V, the transistor shows a backward rectification effect and reverses its direction of rectification in the range 10–15 V. In this way, we achieved simultaneous modulation of the magnitude and direction of rectification in an SMT simultaneously. We propose the new term of "tidal" diode for this device in recognition of this new traffic rule in electronics.

In order to study the temperature characteristics of the device and their influence on the diode rectification effect, we conducted a set of temperature-dependent experiments. Figure 3(a) shows the current as a function of V_g and temperature T for V_{ds} fixed at 2 mV. We extracted three curves of current against T and plotted these in Fig. 3(b). At the degeneracy point $V_g = ~14.5$ V, the current decreases as the temperature increases, while the current increases as the temperature increases in the blockade region at $V_g = 19.2$ V. The current in the conducting region at $V_g = 15.91$ V remains almost constant. Figure 3(c) shows the $I_{ds}-V_{ds}$ characteristics in the blockade region of $V_g = -13.5$ V at different temperatures. The 2D map of the RR as a function of V_{ds} and T in Fig. 3(d) shows that RRs greater than ten are present up to 20 K and remain above 1 up to 60 K. Figure 3(d) maintains the gate voltage at -13.5 V during the measurement.

To explain the origin of the tidal rectification effect in our Au25-R based SMTs, we introduce a resonant tunneling model and take asymmetric coupling into account.²⁻⁴ The Au₂₅-R clusters' core vicinity is designed to contain different elements, such as S, P, and Cl, which tend to form asymmetric couplings that lead to the rectification effect in this case. The strong asymmetry of the coupling between the molecule and each of the electrodes causes the chemical potential of the molecule to be more readily affected by the Fermi level of the electrode to which the molecule is strongly coupled. In Fig. 4(a), the chemical potential of the molecule is shown to rise above the Fermi energy level of two electrodes with no applied bias, and it switches downward or upward respectively, following the Fermi level of the left electrode for a positive or negative bias. Under a negative bias, it is easier for the chemical potential of the molecule to align with the Fermi surface of the right electrode, resulting in resonant tunneling with a large current. However, at positive V_{ds} , it is difficult for the Fermi surface of the left electrode to catch up with the upward shift in the energy level, and the current remains suppressed, resulting in a negative direction of rectification. The direction is reversed when the chemical potential of the molecule is tuned by $V_{\rm g}$ to a position below the Fermi level of the electrodes, as shown in Fig. 4(b).

Based on the Landauer formula and the asymmetric coupling model, 40,41 the derivation gives

$$I(V) = \frac{2e}{h} \frac{4\Gamma_L \Gamma_R}{\Gamma} \bigg[\arctan\bigg(\frac{eV/2 - \epsilon_0}{\Gamma} - \frac{eV(\Gamma_L - \Gamma_R)}{2\Gamma^2}\bigg) + \arctan\bigg(\frac{eV/2 + \epsilon_0}{\Gamma} + \frac{eV(\Gamma_L - \Gamma_R)}{2\Gamma^2}\bigg) \bigg],$$
(1)



FIG. 3. (a) Current as a function of $V_{\rm q}$ and T for $V_{\rm ds}$ fixed at 2 mV. The Coulomb oscillation peak becomes indistinguishable as the temperature increases. (b) Cut lines in (a) for three different Vg values. Three different behaviors can be seen: the current increases, decreases, or stays constant as the temperature is increased. (c) The current as a function of bias voltage at different temperatures. (d) The rectification ratio is a function of temperature and bias voltage. A remarkable amount of rectification can be seen in all the cases shown, although in some areas the magnitude decreases slightly. The rectification effect persists even when the temperature reaches 60 K. The gate voltage in (c) and (d) is set to -13.5 V where the molecule is far away from the resonant point, i.e., in the Coulomb blockade regime.

where *e* is the electron charge, *h* is Planck's constant, Γ_L and Γ_R are the strength of the coupling between the molecule and the two metal electrodes, $\Gamma = \Gamma_L + \Gamma_R$, and ϵ_0 is defined as the energy level at which a molecule is involved in conducting electricity. We fitted the experimental $I_{ds}-V_{ds}$ data using the equation obtained above as depicted in Fig. 5(a) and obtained two fitting parameters $\Gamma_L = 7.7$ meV and $\Gamma_R = 4.9 \times 10^{-2}$ meV with two orders of magnitude of difference. A simulation of the absolute current and RR against V_g and V_{sd} according to the single-level resonant



FIG. 4. (a) and (b) Tunneling process when the resonant energy level is above and below the electrode Fermi energy at zero bias, respectively. The coupling to the left electrode is much stronger than that to the right one, which denotes a thinner tunneling barrier in the left interface.

tunneling model with these fitting parameters shows excellent agreement with the experimental data, as depicted in Figs. 5(b) and 5(c). Therefore, if there is a large difference in the coupling strength between the molecule and the electrodes, the direction of rectification will change on either side of the degeneracy point, which is consistent with the reversal of the direction of rectification shown in Fig. 2(d).

In order to understand the mechanism of temperature dependence of the rectification effect, we focus on the Fermi distribution function of the electrodes in Landauer's formula, written as

$$f_{L,R}(E) = \frac{1}{1 + \exp[(E - \mu_{L,R})/k_BT]},$$
 (2)

where $k_{\rm B}$ is the Boltzmann constant and $\mu_{L,R}$ is the chemical potential of the system. Electrons have a certain probability of occupying states with energy higher than the Fermi energy at a finite temperature. For the resonant region, for example, when electrons tunnel from the left electrode to the molecule and then out from the right electrode, the density of states (DOS) near the Fermi surface on the right electrode decreases, resulting in a reduction in the tunneling current. Figure 5(d) presents the simulated results of the absolute currents as a function of $V_{\rm g}$ and T by numerical calculation of the integrated Eq. (1) at non-zero temperature. It can be seen that the calculated results are in general agreement with the experimental data in Fig. 3(a), with all three different regional features being preserved. There are some differences in the detail, which may be due to the change in the coupling strength of the molecular junction at high temperatures in the experiment.



FIG. 5. (a) Use of the Landauer approach to fit the experimental results. The red dotted-dashed line shows the measured results, and the black line shows the fitted results. A different scattering rate can be obtained. $\Gamma_{\rm L}=7.7$ meV, and $\Gamma_{\rm R}=4.9\times10^{-2}$ meV. (b) A simulation of the experimental results according to the fitting parameter obtained in (a). (c) The calculated rectification ratio is a function of V_g and $V_{\rm ds}$. (d) Simulation of temperature-dependent current behavior according to the Fermi function, which broadens when using the Landauer resonant tunneling model.

In summary, we have shown experimental results for Au_{25} -R based SMTs, where single-electron transport phenomena were observed experimentally, together with a rectification effect with a maximum magnitude of ~30. We also showed that the rectification magnitude and conducting direction of our diodes can be modulated by gate voltage and temperature. To explain how this modulation takes place, a single-level resonant tunneling model was introduced in order to rationalize the experimental results. Results of data fitting and computational simulations corroborate the rationality that the rectification effect originates from the coupling asymmetry.

See the supplementary material for details of chemical synthesis, material characterization, and the temperature effect on the rectification ratio.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Zewen Zuo: Conceptualization (equal); Data curation (equal); Writing – original draft (equal); Writing – review & editing (equal). Weicheng Yan: Conceptualization (equal); Data curation (equal); Writing – original draft (equal). Kangkang Zhang: Conceptualization (equal); Data curation (equal); Writing – original draft (equal). Caigan Xi: Investigation (equal); Validation (equal). Yuewen Mu: Investigation (equal); Validation (equal). Yuewen Mu: Investigation (equal). Validation (equal). Yuewen Mu: Investigation (equal). Minhao Zhang: Conceptualization (equal); Funding acquisition (equal). Supervision (equal); Validation (equal); Writing – review & editing (equal). Kuo-Juei Hu: Supervision (equal); Validation (equal); Writing – review & editing (equal). You Song: Investigation (equal); Validation (equal). Fengqi Song: Conceptualization (equal); Writing – review & editing (equal). (equal); Validation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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