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Charge transport properties of SARS-CoV-2 Delta variant (B.1.617.2)

Lijun He*, Zhiyang Xie, Xing Long, Chaopeng Zhang, Chengyun He, Boyang Zhao, Fei Qi, Nan Zhang

The School of Optoelectronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

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ABSTRACT

The B.1.617.2 (Delta) variant of concern is causing a new wave of infections in many countries. In order to better understand the changes of the SARS-CoV-2 mutation at the genetic level, we selected six mutations in the S region of the Delta variant compared with the native SARS-CoV-2 and get the conductance information of these six short RNA oligonucleotides groups by construct RNA: DNA hybrids. The electronic characteristics are investigated by the combination of density functional theory and non-equilibrium Green’s function formulation with decoherence. We found that conductance is very sensitive to small changes in virus sequence. Among the 6 mutations in the Delta S region, D950N shows the largest change in relative conductance, reaching a surprising 4104.75%. These results provide new insights into the Delta variant from the perspective of its electrical properties. This may be a new method to distinguish virus variation and possess great research prospects.

1. Introduction

SARS-CoV-2 is the virus that causes COVID-19 and B.1.617.2 is one of the variants of SARS-CoV-2 which was first detected in India [1]. B.1.617.2 is also named Delta by WHO (World Health Organization) for easy discussions in the public. The Delta variant acquires multiple mutations which can affect viral properties such as infectivity and immune resistance. For example, it has been reported that L452R (mutation in the 452th amino acid on spike protein from Leucine (L) to Arginine (R)) helps the virus escaping from HLA-A24-mediated cellular immunity and increasing binding affinity to ACE2 [2]. A recent article also pointed out that P681R can make the virus enter cells more effectively [3]. Because of its increase in transmissibility and more severe disease, the Delta variant rapidly spread during the second wave of COVID-19 in India, and it has spread to 78 countries [4].

The continuation of the spread of the highly transmissible SARS-CoV-2 Delta variant points out the significance of virus mutation research. Although a large number of researchers have studied the nature and infectivity of the Delta variant. But so far, few articles have studied the Delta variant from the perspective of it’s electronic characteristics. SARS-CoV-2 is a positive-sense single-stranded RNA virus of about 30,000 base length. In recent years, some studies have studied the charge transport in nanomaterials [5,6] and the electrical properties of cytosine hydroxymethylated (Chm) DNA sequences [7]. A recent article found that single-molecule conductance techniques can be used to extract biologically relevant information from short RNA oligonucleotides by construct RNA:DNA hybrids [8]. So this paper has considered whether virus variation can be analyzed from the perspective of electrical characteristics. In this work, the charge transport properties of the Delta variant sequence with the native SARS-CoV-2 sequence are compared. We demonstrate that the conductance of RNA:DNA hybrids is highly sensitive to single nucleotide differences of Delta variant and native SARS-CoV-2.

2. Materials and methods

2.1. Obtain the sequence information of mutation site before calculation

The SARS-CoV-2 mutates all the time, It has been found that more than 10 mutations have occurred on Delta variant compared with the original SARS-CoV-2 (MN908947.3, one of the initial isolates of SARS-CoV-2 and serves as a reference sequence). But this work focuses on the mutations in its spike (S) protein because the SARS-CoV-2 spike (S) glycoprotein is exposed at the surface of the virus and mediates entry into host cells. S is the main target of neutralizing antibodies and the focus of most vaccines [9,10]. We get the mutation information from the 2019 Novel Coronavirus Resource and collected six of the most critical mutations in the S region [11–13]. The key information of the six

* Corresponding author.
E-mail addresses: helijun4@126.com, helj@cqupt.edu.cn (L. He).

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Table 1
The key information of the six mutations of Delta variant (compared with MN908947.3).

| Genome position | Base change | Gene | Amino acids change | Before mutation | After Mutation |
|-----------------|-------------|------|--------------------|-----------------|----------------|
| 21,618          | C -> G      | S    | T19R               | UUACAC          | UUAGAAC        |
| 22,917          | U -> G      | S    | L452R              | ACCUGUA         | ACCGGUA        |
| 22,995          | C -> A      | S    | T478K              | GCACACC         | GCAAAC         |
| 23,403          | A -> G      | S    | D614G              | AGGAUGU         | AGGGGU         |
| 23,604          | C -> G      | S    | P681R              | CUCUCUG         | CUCUCUG        |
| 24,410          | G -> A      | S    | L452R              | CUCGUG          | CUCGUG         |

Fig. 1. Idealized schematic of electrical property experimental setup. The RNA:DNA hybrids molecule is bounded between two yellow gold electrodes.

2.2. Construct the RNA: DNA hybrid structure

The Nucleic Acid Builder (NAB) software package can be used to construct various nucleic acid structures. Research has found that the RNA: DNA hybrid molecules are all in an A-form-like configuration, so we first constructed A-form-RNA and A-form-DNA according to the above virus sequence, and then combined them into RNA: DNA hybrid structure by NAB. It is worth noting that in this work, we study the charge transport of pure static nucleic acids without considering the influence of counter ions.

2.3. DFT and non-equilibrium Green’s function

After obtaining the RNA: DNA hybrid molecular structure of virus sequences, the density functional theory (DFT) and non-equilibrium Green’s function approach including decoherence [14–17] are employed to calculate the electrical information of different molecular structures. First of all, the DFT calculations were performed by Gaussian09 [18] and we chose B3LYP functional and 6–31 G (d, p) basis set. In order to be closer to the real experimental environment, the polarization continuum model (PCM) is used to consider the influence of solvent (water). After DFT calculations we will obtained the Hamiltonian and the overlap matrices of the calculated molecular structure and then use Löwdin transformation [19] method to convert it into orthogonalized Hamiltonian matrix.

So far, we have obtained the orthogonalized Hamiltonian matrix of the system by using DFT, next, the Hamiltonian matrix is calculated to obtain the electrical information such as conductance, transmission probability of virus sequence by the non-equilibrium Green’s function formulation with decoherence. The retarded Green function can be calculated by:

\[
G_{\text{eff}}(E) = \frac{1}{E I_{\text{SM}} - H_{\text{SM}} - \sum_{i}^{} - \sum_{r}^{} - \sum_{b}^{} + \Gamma_{\text{eff}}(E)}
\]  

Where \( E \) is the energy, \( I_{\text{SM}} \) is identity matrix of M*M, \( H \) is the Hamiltonian of the molecule, \( \sum_{i}^{} \) and \( \sum_{r}^{} \) are the self energy matrices from the left (right) contact. In order to incorporate decoherence into the transmission model, \( \sum_{b}^{} \) is used to represents the self energy matrices generated by the Buttiker probes.

The transmission probability can be obtained by:

\[
T_{\text{eff}} = \Gamma_1 G^r \Gamma_2 G^a + \sum_{ij=1}^{N_p} \Gamma_1 G^r \Gamma_i G^a W_{ij}^{-1} \Gamma_i G^a \Gamma_j G^r
\]

Where \( \Gamma_i(R) \) is the coupling between the Intermediate molecule and the left or right contacts. Here, contact coupling between the molecule and the two electrodes is set to 100 meV. \( G^r \) is the retarded Green functional in Eq. (1), \( G^a \) is the advanced Green functional. \( N_p \) represents the number of Buttiker probes. The \( W_{ij} \) is the inverse of \( W_{ij} = [(1-R_{ab})\delta_{ij}]^{-1} \Gamma_i \Gamma_j \Gamma_i \Gamma_j \Gamma_i \Gamma_j \), where \( R_{ij} \) is the reflection probability at probe \( i \).

In this article, the decoherence rate is set to 10 meV.

After obtaining the transmission probability, the conductance of the molecule can be obtained by:

\[
G(E_F) = G_0 \int dE T_{\text{eff}}(E) \left(-\frac{\partial f(E - E_F)}{\partial E}\right)
\]

Where \( E_F \) is the Fermi functional, \( G_0 \) is The quantum conductance and \( G_0 = 2e^2/h \approx 7.75 \times 10^{-5}\) S. \( T_{\text{eff}} \) is the transmission probability we have calculated above.

In our previous publication, we have define a parameter to better understand the relative change in conductance upon mutation [20]. Here, we also use \( G_{\text{to}} \) make it more intuitively to shows the change of conductivity before and after virus mutation, where \( G_{\text{to}} \) represents the conductance of the naive sars-cov-2 and \( G_{\text{mut}} \) represents the conductance of the Delta variant.

\[
\delta G = \frac{G_{\text{mut}} - G_{\text{to}}}{G_{\text{to}}} \times 100
\]

Fig. 1. Idealized schematic of electrical property experimental setup. The RNA: DNA hybrids molecule is bounded between two yellow gold electrodes.
3. Results and discussion

For the convenience of discussion, we will use amino acid changes to refer to specific virus sequences in the following analysis, such as pre-D614G (pre-mutation) represent the sequence of AGGAUGU and D614G represent the sequence of AGGGUGU (refer to Table 1). Fig. 2 shows the conductance variation with energy in the vicinity of respective HOMO (Highest Occupied Molecular Orbital) energy for the six mutation sites of the Delta variant. It is easy to see that compared with the native SARS-CoV-2 sequence, the conductance of the Delta variant has changed significantly in all six mutation cases. The conductance variation of pre-T19R and T19R is shown in Fig. 2a. In this mutation, a C base is changed to G base. After mutation, the conductance increased from $2.00 \times 10^{-5} G_0$ to $1.52 \times 10^{-4} G_0$, that is, $\delta G = 660\%$. Fig. 2b shows the conductance of pre-L452R and L452R. Same as T19R, after mutation, the conductance of L452R increased from $6.84 \times 10^{-6} G_0$ to $7.43 \times 10^{-6} G_0$, the change is only 8.63\%, which is the minimum conductance change among all the six mutations studied. Fig. 2c presents the conductance variation of virus sequence when a C base is changed to A base. The conductance decreased from $1.05 \times 10^{-5} G_0$ to $3.42 \times 10^{-6} G_0$, that is, $\delta G = 67.43\%$. We can see that there are three successive AT base pairs in the Delta sequence after mutation and there have been research findings that AT base pair acts as a barrier and GC base pair as a well for hole transport in DNA (dsDNA) duplexes [21]. So we believe that AT base pair has the same barrier properties in RNA:DNA hybrids as dsDNA. Fig. 2d shows the conductance variation of pre-D614G and D614G. The conductance variation of pre-D614G and D614G represent the sequence of AGGAUGU and D614G represent the sequence of AGGGUGU (refer to Table 1). Fig. 2 shows the conductance variation with energy in the vicinity of respective HOMO (Highest Occupied Molecular Orbital) energy for the six mutation sites of the Delta variant. It is easy to see that compared with the native SARS-CoV-2 sequence, the conductance of the Delta variant has changed significantly in all six mutation cases. The conductance variation of pre-T19R and T19R is shown in Fig. 2a. In this mutation, a C base is changed to G base. After mutation, the conductance increased from $2.00 \times 10^{-5} G_0$ to $1.52 \times 10^{-4} G_0$, that is, $\delta G = 660\%$. Fig. 2b shows the conductance of pre-L452R and L452R. Same as T19R, after mutation, the conductance of L452R increased from $6.84 \times 10^{-6} G_0$ to $7.43 \times 10^{-6} G_0$, the change is only 8.63\%, which is the minimum conductance change among all the six mutations studied. Fig. 2c presents the conductance variation of virus sequence when a C base is changed to A base. The conductance decreased from $1.05 \times 10^{-5} G_0$ to $3.42 \times 10^{-6} G_0$, that is, $\delta G = 67.43\%$. We can see that there are three successive AT base pairs in the Delta sequence after mutation and there have been research findings that AT base pair acts as a barrier and GC base pair as a well for hole transport in DNA (dsDNA) duplexes [21]. So we believe that AT base pair has the same barrier properties in RNA:DNA hybrids as dsDNA. Fig. 2d shows the conductance variation of pre-D614G and D614G. The
Table 2
The transmission, conductance, under the six mutations of the Delta variant.

| Virus  | Sequence       | HOMO (eV) | Cond $(G_0)$ | Teff (HOMO) | δG  |
|--------|----------------|-----------|--------------|-------------|-----|
| pre-T19R | UUACAAC       | -5.07     | 2.00E-05     | 1.77E-05    | 660%|
| T19R   | UUAGAAC       | -5.12     | 1.52E-04     | 7.01E-05    | 8.63%|
| pre-L452R | ACCUGUA    | -4.89     | 6.84E-06     | 6.77E-06    | 6.3% |
| L452R  | ACCGGUA       | -4.86     | 7.43E-06     | 9.29E-06    | 57.43%|
| pre-   | GCACACC       | -4.78     | 1.05E-05     | 2.68E-05    | 78.23%|
| D614G  | AGGGUGU       | -4.88     | 7.27E-06     | 1.61E-05    | 4104.75%|
| pre-P681R | CUCUCUC    | -4.92     | 1.52E-05     | 1.47E-05    | 55.33%|
| P681R  | CUGCUCCG      | -4.82     | 6.79E-06     | 6.56E-06    | 58.63%|
| pre-   | CAAAGUG       | -4.77     | 5.47E-06     | 4.90E-06    | 4104.75%|
| D950N  | CAUAAGU       | -4.72     | 2.30E-04     | 7.60E-04    | 100% |

conductance at HOMO before the mutation is $3.34 \times 10^{-5}$ $G_0$ and $7.27 \times 10^{-6}$ $G_0$ after the mutation, that is, $\delta G = -78.23\%$. The reason why the conductance becomes smaller after mutation is the pre-D614G possesses higher HOMO decreasing the activation energy for a charge to move between the electrodes and the bridge [8]. In Fig. 2f, we can obviously see that the conductance of the virus changes much more before and after mutation compared with the other five cases. The $\delta G$ value reached a surprising $4104.75\%$. This shows that it is more possible to detect this mutation by measuring sequence conductance. To provide additional verification that why D950N possesses higher conductance than pre-D950N, here we also performed ab initio electronic structure calculations of the 7 bp RNA:DNA duplex using the Gaussian 09 W software package and the Multiwfn [22] to examine the delocalization of the HOMO level along with the base stack. Fig. 3 plots the HOMO isosurface (isovalue $= 3 \times 10^{-3}$). Fig. 3a and Fig. 3b represent the HOMO isosurface of pre-D950N and D950N, respectively, and in Fig. 3 it is evident that a higher delocalization of the HOMO orbital in the D950N case. These results suggest that for a given number of bp’s, the charge should transport more efficiently in the D950N case than in the pre-D950N case [23]. This fact is consistent with the conductance we calculate before.

4. Conclusion

In this work, we have investigated the electronic characteristics of Delta variant and native SARS-CoV-2 sequence by a combination of DFT and non-equilibrium Green’s function including decoherence. These results provide new insights into the ongoing second wave of COVID-19. We demonstrate that the conductance is extremely responsive to small changes in the virus sequence, down to single-base modification. The underlying reason for this specificity originates may attribute to their conformational differences due to viral mutations. We have plots the HOMO isosurface which show that the HOMO level is more distributed along with the molecules in RNA:DNA duplexes of D950N, which suggests a higher conductance than pre-D950N. Given the obvious difference of conductance caused by mutation, this electrical measurement of SARS-CoV-2 may open the new door to single-molecule sensors with applications in fundamental biomedical research and COVID-19 diagnosis.

Data accessibility

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

Data availability

Data will be made available on request.

Fig. 3. 3D iso-surface plot of the HOMO orbital: (a) pre-D950N and (b) D950N, (blue and red colors represent positive and negative isosurfaces, respectively; isovalue $= 3 \times 10^{-3}$).
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