Graphene electrochemistry: edge vs. basal plane sites

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Abstract. This work is focused on the topic of electrocatalytic activity of graphene edges. DFT calculations and quantum mechanical theory of charge transfer is used for the investigation of heterogeneous electron transfer kinetics by the example of the oxygen reduction reaction, which is important for electrochemical applications. It is shown that the rate of electron transfer at zig-zag edges is ~4 times larger than far from edges. Electron transfer occurs in nonadiabatic regime all over the graphene cluster at distances greater than 5Å. The highest occupied molecular orbital of the graphene cluster makes the main contribution to the electron transfer. Electrocatalytic effect of zig-zag edges is explained by preferential localization of the highly occupied molecular orbital on edges.

1. Introduction

Investigation of the heterogeneous electron transfer (ET) at the graphene surface is highly relevant today due to the perspectives of graphene use in electrochemical energy-storage devices [1]. Electrochemical properties of defective graphene is of particular interest by virtue of the fact that point and linear defects show high electrocatalytic activity [2, 3]. This effect is potentially useful for the development of cheap and catalyst-free graphene-based electrodes for electrochemical applications.

Kinetics of the redox processes at the graphene edge (linear topological defect) is mostly studied but controversial field. It was stated that the rate of ET at the edges is faster than at basal plane of graphite and sidewall of nanotubes [4, 5], and the latest delicate experiment on a single-layer graphene sheet confirmed it [3]. But on the other side, this effect was not reproduced and disputed by others [6, 7].

Important data for interpretation of this electrocatalytic effect was obtained theoretically in Fujita’s work where it was shown the existence of the electronic states, which are strongly localized on zig-zag edges and have the energies near the Fermi level [8] (confirmed experimentally in [9]). According to the Gerischer model such states have the highest contribution to the ET rate. In our previous works, we have shown that the surface electronic properties, the rate of redox processes also depends on the electrode/electrolyte interface structure [10]. In particular, the distributions of the redox-active components and the barriers for their adsorption are different at the edge and the basal plane sites [11-14], which is another possible factor determining the catalytic activity.

Despite of many works on the subject, there is a lack of quantitative calculations of the ET kinetics on the graphene edges, which could allow to separate contributions of different factors to the redox processes. The aim of this work is quantitative analysis of the effect of surface electronic properties on the ET rate by calculating the electronic transmission coefficient near and far from zig-zag edge. The transmission coefficient represents the probability of the ET from the surface to the reactant in solutions.
when donor and acceptor levels are aligned. The calculations have been performed for the oxygen reduction reaction \( O_2 + e^- \rightarrow O_2^- \), which is one of the key processes in fuel cells and metal-air batteries.

2. Computational details

The calculations were carried out for the graphene fragment \( C_{150}H_{30} \) with zig-zag edges terminated by hydrogen atoms (figure 1). We studied the electron transfer from the \( C_{150}H_{30} \) molecule to the \( O_2 \) molecule located above different points near and far from edge perpendicularly to the surface. At the same time, the distance from the oxygen molecule to the graphene surface was scanned.

Since we used cluster model, the surface has a discrete energy spectrum. In this case the rate constant of ET equals [10, 15-18]:

\[
k = \sum_{i=1}^{N} \frac{\omega_{\text{eff}}}{2\pi} \kappa^{(i)} \exp \left( \frac{(\lambda + \epsilon_F - \epsilon_{\text{HOMO}})^2}{4\lambda kT} \right)
\]

(1)

where \( \kappa^{(i)} \) is the electronic transmission coefficient from \( i \)-th orbital of the surface to the acceptor molecular orbital; \( \lambda \) is the reorganization energy of solvent; \( \epsilon_F \) is the Fermi level of electrode, i.e., the highest occupied molecular orbital (HOMO) of the cluster; \( \epsilon_{\text{HOMO}} \) and \( \eta \) are the electron charge and the overpotential respectively, \( \omega_{\text{eff}} \) is the polarization frequency. Since the oxygen being in triplet state \( 3\Sigma_g^+ \) has two degenerate single occupied molecular orbitals (SOMOs), we calculated maximum of coupling between cluster’s orbitals and both of SOMOs. We used typical values of the reorganization energy and the polarization frequency, which are equal to 50 kcal/mol and \( 10^{13} \text{s}^{-1} \) respectively [10].

We used the Landau-Zener theory [19-21] for the transmission coefficient calculations, which can be estimated from the following equation in the nonadiabatic limit [10, 16]:

\[
\kappa^{(i)} \approx \frac{2\pi}{\hbar \omega_{\text{eff}}} H_{if} \left( \frac{\pi}{kT} \right) \int \psi_i \hat{H}_{if} \psi_f d\Omega.
\]

(2)

where \( H_{if} \) is the electronic coupling matrix element: \( H_{if} = \int \psi_i \hat{H} \psi_f d\Omega \). To calculate \( H_{if} \) we used method based on the linear correlation between the electronic coupling matrix element and the overlap between corresponding orbitals: \( S_{if} = \int \psi_i \psi_f d\Omega \) [22]. Idea of this approach originates from Hückel theory [23].

\[
H_{if} \approx CS_{if}
\]

(3)

Constant \( C \) was obtained from the model problem of the electron transfer from benzene to the oxygen molecule, comparing the overlap integral of the benzene HOMO and the oxygen SOMOs and the electronic coupling matrix element calculated within the framework of the generalized Mulliken-Hush (GMH) [24].

Density functional theory (DFT) level was used to obtain the molecular orbitals of graphene cluster and oxygen molecule. We used B3LYP hybrid functional and 6-31G basis set. Configuration of the graphene cluster was built using Atomic Simulation Environment (ASE). Visualization of the electronic density were obtained using VESTA [25].

3. Results and discussion

Since there is a difference between the Fermi level and the level of \( i \)-th molecular orbital in exponential part of the equation (1), the HOMO has the highest contribution to the kinetics of heterogeneous electron transfer. The next energy level (HOMO-1) is 0.4 eV lower than the HOMO level. In case of zero overpotential this leads to a decrease of the contribution from this orbital by 3 orders of magnitude. So, we can ignore all the orbitals below the HOMO when analyzing ET kinetics. Figure 1 depicts the distribution of the electronic density from the HOMO of the graphene cluster. One can see preferential localization of the electronic density on zig-zag edges of graphene.
Figure 1. Distribution of the electronic density from HOMO

Figure 2. Electronic transmission coefficient as a function of the distance to the graphene surface opposite points A-G depicted in figure 1

Figure 2 shows the electronic transmission coefficient as a function of the distance to the graphene surface opposite the characteristic points, depicted in figure 1. The distance was scanned from 5 to 6.5 Å. One can observe the exponential decay of the transmission coefficient with distance, which agrees with previous theoretical studies on other redox systems [10] and experimental observations [26]. Transmission coefficient values are much smaller than 1 indicating that ET occurs in the nonadiabatic regime all over the graphene cluster at such distances. The highest electronic transmission coefficient is observed in point A – the midpoint of the segment connecting the outer carbon atoms of zig-zag graphene edge. The highest transmission coefficient over the basal plane of the graphene cluster is observed in the hollow position (point E). The maximum value at the edge exceeds the maximum value at basal plane sites by 4 times. For remaining points (B, C and D) at the edge, the values of the transmission coefficient also exceed interior values.

Our results clearly support the dominate thinking in this field that zig-zag edges exhibit electrocatalytic properties. This effect is in agreement with many experimental works [3-5]. As for other works where the effect was not confirmed we propose the following possible explanations [6, 7]. It may be associated with 1) variety graphene edges morphology in experiments such as armchair edges, which does not have localized states in contradiction to zig-zag ones [8, 9]; 2) defects on the edges, in the presence of which local states are suppressed [9, 27]; 3) and various functional groups terminating edges, which can also strongly influence the electronic properties of graphene [28].

4. Conclusion
In this work we investigated the effect of zig-zag graphene edge on the kinetics of the heterogeneous electron transfer. It was observed, that the highest occupied molecular orbital has the greatest contribution to the kinetics of electron transfer. Distribution of electronic density from the HOMO of the graphene cluster was calculated. We observed the preferential localization of the electronic density on zig-zag edges of the graphene. The electronic transmission coefficient representing the probability of the electron transfer from the graphene to the oxygen molecule was calculated opposite the characteristic point at the edge and the basal plane sites of the graphene cluster. The 4 times increase in the maximum of transmission coefficient at the edge compared to the basal plane was found. We observed the catalytic effect of the zig-zag edge of graphene for the heterogeneous electron transfer on the oxygen molecule as one of the key stages of the oxygen reduction reaction in fuel cells and metal-air batteries.
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