

Electronic Supplementary Information

**Effect of Au underlayer on outer-sphere electron transfer across the  
Au/graphene/electrolyte interface.**

Sergey A. Kislenko<sup>a,\*</sup>, Sergey V. Pavlov<sup>b,a</sup>, Renat R. Nazmutdinov<sup>c</sup>, Vitaliy A. Kislenko<sup>b,a</sup>,

Petr M. Chekushkin<sup>a</sup>

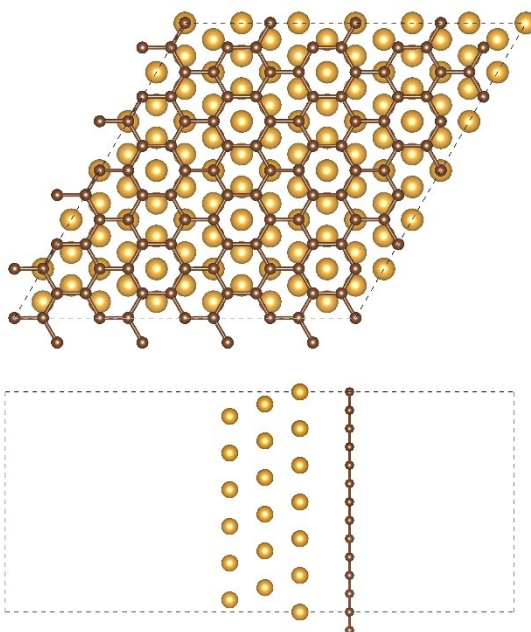
<sup>a</sup> Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13/2,  
Moscow, 125412, Russian Federation

<sup>b</sup> Skolkovo Institute of Science and Technology, Nobel Str. 3, Moscow, 143026, Russian  
Federation

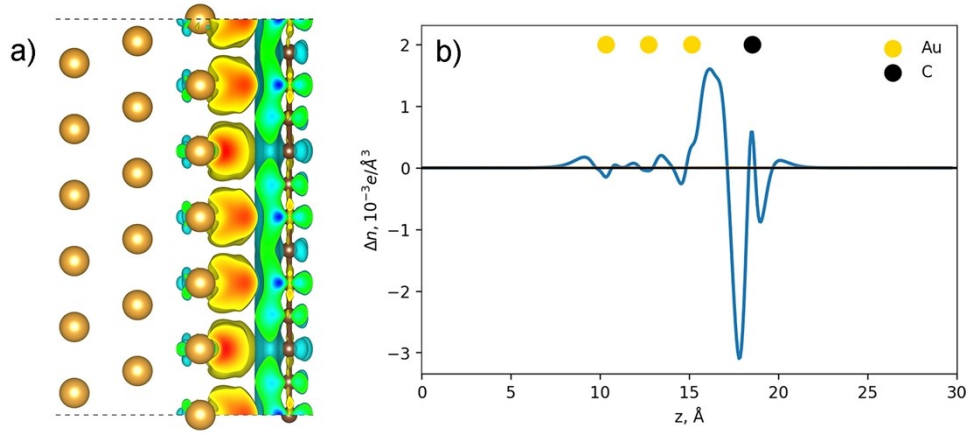
<sup>c</sup> Kazan National Research Technological University, R. Marx Str. 68, 420015 Kazan, Republic of  
Tatarstan, Russian Federation

\* Corresponding authors. *E-mail address*: [kislenko@ihed.ras.ru](mailto:kislenko@ihed.ras.ru) (S.A. Kislenko).

**1. Periodic DFT calculations.**



**Fig. S1.** Snapshot of the Au(111)/graphene system (top and side views).



**Fig. S2.** (a) - charge density difference for the Au/graphene system; (b) - planar averaged charge density difference plot.

We used periodic plane-wave DFT simulations with the projector augmented wave (PAW) formalism as implemented in the Vienna Ab Initio Simulation Package (VASP) [1]. Generalized gradient approximation (GGA) for the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) was used [2]. After preliminary calculations of bulk Au crystal using different Van der Waals corrections (see Table S1), we chose the zero damping DFT-D3 method of Grimme. This method gives the best match of the calculated Au lattice constant with the experimental one, which are 4.099Å and 4.078Å, respectively.

We used (6x6)-GR30° geometry of graphene-Au(111) system (as shown in the fig. 1S) to represent graphene layer on Au(111) substrate. The computational cell was extended along the z-axis to 35Å to minimize interactions between periodical images. For the geometry optimization, we used the RMM-DIIS algorithm [3] with  $\Gamma$ -point approximation and both electronic and ionic convergence criteria of  $10^{-5}$ eV. The optimized distance between the graphene layer and Au(111) surface was 3.38Å, which is consistent with previous works [4–7].

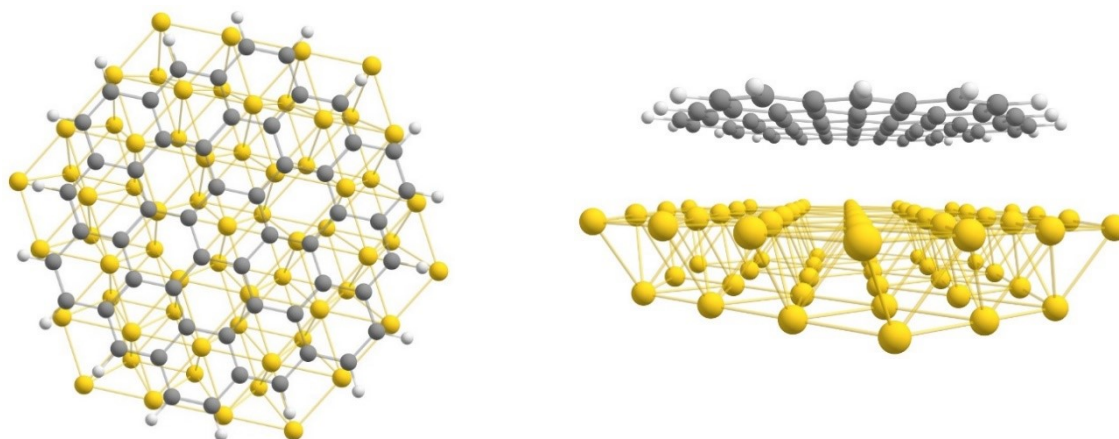
To calculate the electronic structure of the graphene/Au(111) system, which is used for further electron transfer calculations, we increased the Brillouin zone sampling to 7x7x1 Monkhorst-Pack k-points mesh. The electronic convergence criterion was  $10^{-6}$  eV. In all calculations, plane-wave cutoff energy was set as 600 eV.

**Table S1.** Au lattice constant calculated using PBE exchange-correlation functional and different VdW corrections in comparison with the experiment.

Method	Au lattice constant, Å	Mismatch with the experiment, Å
Experiment [8]	4.078	0
no correction	4.156	0.078
DFT-D2	3.996	-0.082
Tkatchenko-Scheffler	4.112	0.034
<b>DFT-D3, zero damping</b>	<b>4.099</b>	<b>0.021</b>
DFT-D3, Becke-Jonson damping	4.101	0.023
dDsC dispersion correction method	4.121	0.043
Tkatchenko-Scheffler method with iterative Hirshfeld partitioning	4.113	0.035
Many-body dispersion energy method	4.115	0.037

vdW-DF	4.246	0.168
vdW-DF2	4.342	0.264

## 2. Cluster DFT calculations.



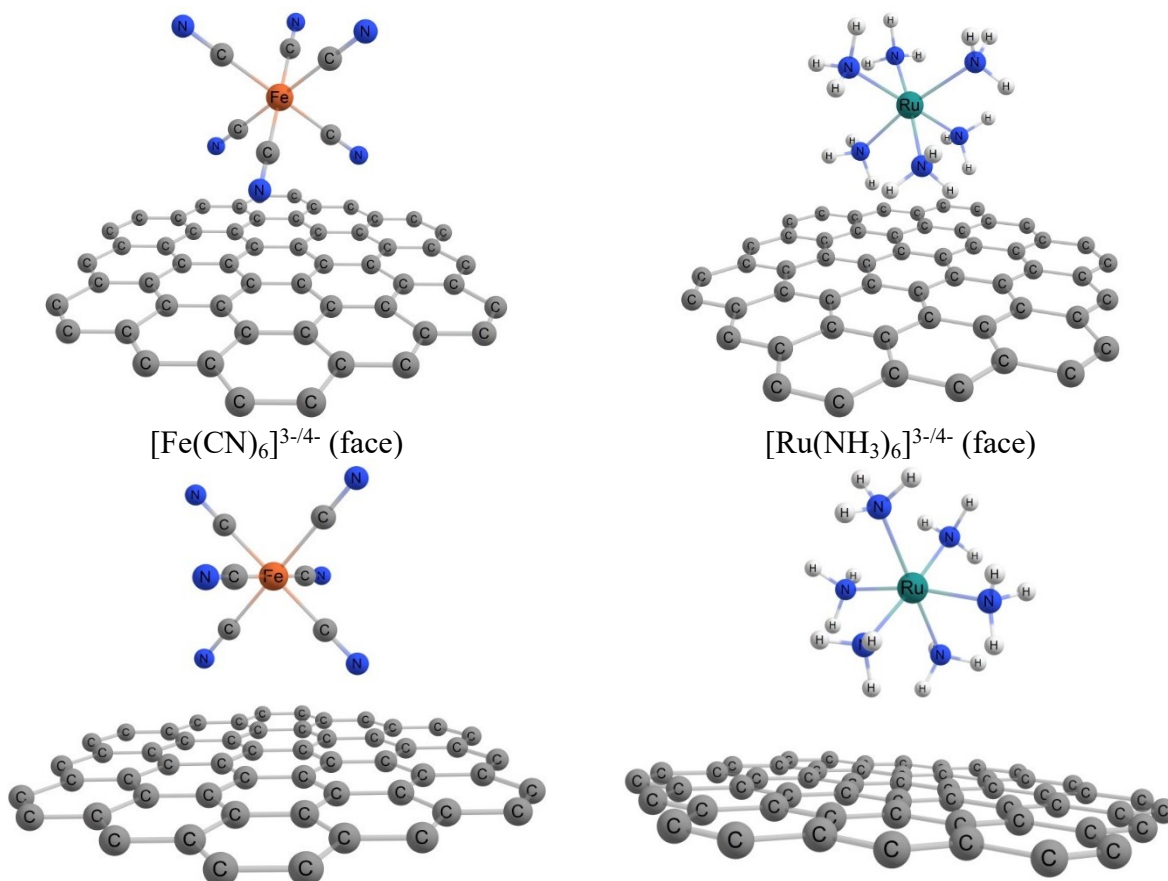
**Fig. S3.** A model  $\text{Au}_{64}(37+27)$  cluster with a coronene molecule ( $\text{C}_{54}\text{H}_{18}$ ) modeling the  $\text{Au}(111)$ /pristine graphene interface: top view (left) and side view (right).

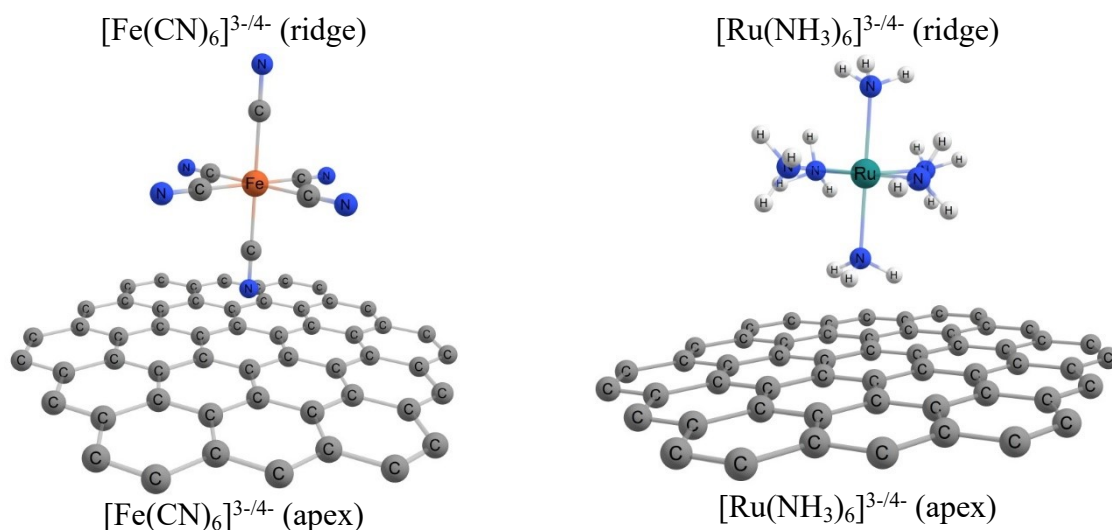
The cluster DFT calculations were performed using the long-range corrected wB97X [9] hybrid functional as implemented into the Gaussian 16 software package [10]. The choice of such a functional seems to be reasonable in order to model a metal electrode/graphene interface. Another hybrid functional b3pw91 [11,12] was used in a set of test calculations as well. The  $\text{Au}(111)$  electrode surface was described by a two-layer  $\text{Au}_{64}(37+27)$  cluster; a coronene molecule ( $\text{C}_{54}\text{H}_{18}$ ) served as a model for pristine graphene (Fig. 2S). The separation between the metal surface and the graphene plane is 3.38 Å; this value was obtained previously from slab DFT calculations. A double-split basis set (DZ) was employed to describe the valence orbitals of the Au, Fe and Ru atoms, while their internal electrons were treated by the Hay-Wadt relativistic core potential (LanL2) [13]. The standard 6-31g (d, p) basis was used for the O, N, C, and H atoms. To avoid time-consuming calculations, the terminal H atoms in the coronene molecule ( $\text{C}_{54}\text{H}_{18}$ ) were described by a more simple 4-31g basis set. Calculations of the electronic transmission coefficient ( $\kappa_e$ ) rest on a model approach based on the perturbation theory and developed earlier [14]; an original code was used as implemented in the Mathematica 8 software package. The ChelpG method was employed to calculate the atomic charges of complexes in the oxidized (initial) state<sup>1</sup>. Several selected orientations of the reactants relative to the electrode surface are portrayed in Fig.

<sup>1</sup> The electrostatic potential of reactant was assumed as the perturbation operator.

3S. The distance from the metal surface to the complex reactants was scanned with some step. At each distance the position of the central atom of the complex initially projected to the cluster (coronene molecule) center was also scanned in a square  $1.6 \text{ \AA} \times 1.6 \text{ \AA}$  (16 points) parallel to the electrode plane in order to address the surface corrugation. Then the mean average was taken as a resulting  $\kappa_e$  value for a given electrode - reactant distance. In the additional calculations performed by using the b3pw91 functional the electronic transmission coefficients for both redox couples were found to be even smaller than those obtained by the use of wB97X functional. However, this computational level do not change all qualitative trends observed previously for both reactants.

Open-shell systems were addressed in terms of the spin-polarized formalism. It is well known that the ground spin state for both complex species is duplet (oxidized form) and singlet (reduced form) and our calculations accord with these results. The geometry of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  complexes was optimized without symmetry constraints. True energy minima were identified by the absence of negative values of the frequencies of normal vibrations. When calculating the electronic structure of complexes, solvation was taken into account in the framework of the Polarizable Continuum Model (PCM). The effect of the electrode surface on the geometry and electronic structure of the complex reactants was neglected. The geometry and molecular orbitals of the complexes were visualized by the Chemcraft program (<https://www.chemcraftprog.com>).





**Fig. S4.** Three different orientations of two redox-couples relative the electrode surface (only the fragment of graphene layer is shown for simplicity).

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