



Full Length Article

Graphene field-effect transistor sensor for detection of urea in water: Experimental study and DFT analysis

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ARTICLE INFO

Keywords:

DFT
Graphene
Water
Urea
Sensor
FET
Charge transfer

ABSTRACT

Urea sensors are used in medicine for disease monitoring, the automotive industry for emission control, agriculture and food safety for fertilizer and residue analysis, environmental monitoring for water pollution detection, and in industrial processes for production control. This article presents a pioneering experimental study of non-selective urea detection in aqueous solution using graphene doping in a field-effect transistor (FET) configuration. It is demonstrated that water itself p-dopes graphene, while the addition of urea weakens this effect (resulting in reduced p-doping). The response is explained by original density functional theory (DFT) calculations considering the common influence of water and urea. Analyses of charge redistributions and band structures indicate the formation of non-doping urea–water complexes responsible for the observed results. Moreover, the calculations provide deeper insight into the complex urea–water–graphene interactions, which may be utilized in other applications.

1. Introduction

The detection of urea ($\text{CO}(\text{NH}_2)_2$) is crucial in various fields, including medicine, environmental science, and industry. In medicine, urea is an important biomarker for diagnosing and monitoring kidney and liver diseases [1]. In environmental science, high concentrations of urea can indicate water pollution, which can negatively impact ecosystems [2]. In industry, urea is used in various chemical processes, and its accurate detection is essential for quality control and production efficiency [3]. An important intersection between environmental science and industry is the use of urea as a fuel additive in diesel engines in the automotive industry. This approach typically reduces nitrogen oxide emissions by 30–50% under normal operating conditions [4], and potentially achieving reductions close to zero under optimal conditions [5].

Graphene field-effect transistors (GFETs) represent a promising technology for urea detection due to their high sensitivity and their rapid, gate-tuneable response. The main advantages of GFETs include their ability to detect ultra-low concentrations of analytes [6] and the potential for sensor miniaturisation [7]. However, GFETs can be

sensitive to environmental interference [8] and their production can be costly and technologically demanding [9].

Previous experiments on urea detection in aqueous solutions using selective GFETs have demonstrated a high sensitivity and selectivity. These studies have shown that GFETs functionalized with enzymes can detect urea at micromolar concentrations [10,11], which is sufficient for medical applications. However, some experiments have also highlighted issues with long-term stability and measurement reproducibility, especially for higher urea concentrations [7], which are crucial for industrial applications.

Density functional theory (DFT) calculations have provided valuable insights into the interactions between a single urea molecule and graphene [12]. These studies have shown that urea can transfer charge to graphene, affecting its electrical properties. DFT calculations have also revealed how the structure of urea changes in the presence of water [13], which is essential for understanding the behaviour of urea in biological and environmental samples.

In this work, we present an experimental study of a non-selective graphene field-effect transistor (GFET)-based urea sensor specifically designed for industrial applications involving high urea concentrations.

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This approach is distinctly different from most previously reported sensors that focus on highly selective detection at nanomolar levels for biomedical use. Unlike these medical sensors, our device is optimized for robustness and functionality in chemically complex, high-concentration environments typical of industrial settings. This experimental approach is complemented by density functional theory (DFT) calculations, which, in contrast to prior studies focusing solely on isolated urea molecules, model the interaction of urea with the graphene surface in the presence of water. These simulations reveal both structural and electronic properties—such as charge transfer and band structure modulation—of realistic aqueous urea configurations, thereby providing more relevant insights into the sensor's operation under industrial conditions.

2. Methods

The GFET biosensor consisted of a graphene monolayer grown by chemical vapour deposition (CVD), which was transferred onto gold electrodes prepared by UV lithography and electron beam evaporation of Ti (5 nm) / Au (100 nm) on a SiO₂ (285 nm) / Si(100) substrate. The prepared chip was wire-bonded onto a chip expander to facilitate the electrical connections to the measurement units, as shown schematically in Fig. 1a. The graphene channel length between the electrodes was 0.9 mm, and channel width was 1 mm corresponding the sensor sensing area. The electrode spacing was 0.5 mm. The constant current $I = 500$ nA was supplied by the Keithley AC and DC Current Source 6221 between the gold electrodes and the voltage across the graphene layer was measured by the Keithley 2182A Nanovoltmeter. A second Keithley AC and DC Current Source 6221 was used to apply the gate voltage V_G between the silicon substrate and the graphene layer by flowing the gate current I_G through a gate resistor $R_G = 1$ MΩ. During the measurement, the gate voltage was swept from 0 V to 80 V and back to 0 V.

The calculations were performed using the Vienna Ab initio Simulation Package (VASP) [14–16]. Projector Augmented-Wave (PAW) pseudopotentials [17,18] were employed to describe the interaction between the core and valence electrons. To incorporate van der Waals interactions, the optB86b exchange-correlation functional was used [19, 20]. The plane-wave basis set was utilized with a cut-off energy of 800 eV to ensure the accuracy of the results. The Brillouin zone was sampled using a $3 \times 3 \times 1$ Gamma-centred mesh [21]. For the optimization of atomic positions, a maximum force criterion of 0.01 eV/Å was applied. For the calculation of graphene with adsorbed structures, a 6×6 supercell was used for a single urea molecule, while 8×8 supercells

were employed for the other structures to avoid interactions between adsorbates in neighbouring cells. A vacuum space of 18 Å was chosen between graphene layers to prevent interlayer interactions.

From an energetic point of view, two types of energy differences were defined. The first was the adsorption energy, defined as

$$E_{ad} = (E_G + E_{str}) - E_{sys}, \quad (1)$$

where E_G is the calculated energy of the graphene layer itself, E_{str} is the energy of the adsorbing structure itself (i.e., a urea molecule and water–urea complexes), and E_{sys} is the energy of the entire system, i.e., the *graphene + adsorbed structure* system.

The second was the formation energy, calculated as follows

$$E_{form} = (E_G + N_u E_u + N_w E_w) - E_{sys}, \quad (2)$$

where N_u is the number of urea molecules, N_w is the number of water molecules, E_u is the energy of a single urea molecule, and E_w is the energy of a single water molecule.

The adhesion energy describes a process in which all molecular components are already bound together prior to adsorption and subsequently adsorb onto the graphene surface as a pre-formed structure. It is therefore defined as the energy difference between the graphene system with a pre-formed, non-adsorbed structure and the fully adsorbed system. Thus, the adhesion energy assumes that the molecular complexes are formed in the aqueous solution before adsorption onto graphene.

In contrast, the formation energy describes a process in which all molecular components bind together only after adsorption on the graphene surface. It is defined as the energy difference between graphene with separated, non-interacting molecules and the fully adsorbed system. Consequently, adding the formation energy would correspond to desorption into individually non-bonded molecules in the gas phase.

The charge transfer was calculated using Bader charge analysis [22–25], which assigns charge to a given atom according to the minima in the charge density distribution. The Bader analysis was performed on the difference in the charge distribution before and after adsorption

$$\rho_{diff} = \rho_{sys} - (\rho_G + \rho_{str}), \quad (3)$$

where ρ_{sys} is the charge distribution after the interaction of molecules with graphene, ρ_G is the electron charge distribution of pristine graphene, and ρ_{str} is the electron charge distribution of the interacting molecules.

The Boltzmann-weighted charge transfer was calculated as

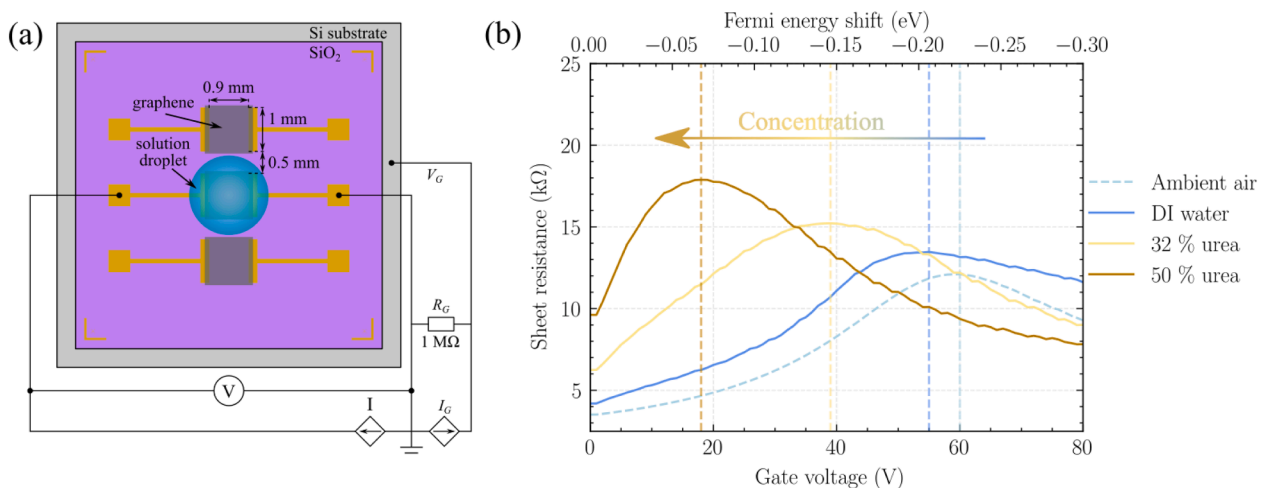


Fig. 1. (a) Schematic of the GFET biosensor interconnected to an electronic measurement setup. The graphene sensing area between the gold electrodes is 0.9×1 mm² with lateral spacing between neighbouring sets of electrodes of 0.5 mm. (b) Measured response of graphene to DI water, 32% and 50% urea concentrations during the forward gate voltage sweep.

$$\Delta Q_j = \sum_{i=1}^{N_j} w_i \Delta Q_i, \quad (4)$$

where ΔQ_j is the Boltzmann weighted charge transfer for j -th urea-to-water molecular ratio, $w_i = \exp(-E_i/(k_B T))/Z$, where E_i is the energy of i -th structure, k_B is the Boltzmann constant, $T = 300$ K is the temperature, and Z is the canonical partition function. ΔQ_i is the charge transfer of the i -th structure of graphene-water-urea system calculated using Bader charge analysis on the charge distribution ρ_{diff} , and N_j is the number of structures for the given urea-to-water molecular ratio.

3. Results and discussion

3.1. Experiment

A 10 μ L droplet of deionized (DI) water (the reference solution) was pipetted onto the graphene sensing area, and then the sensing experiment was carried out. After the measurement, the droplet was removed by a pipette, and the graphene layer was left to dry. The procedure was subsequently repeated for 32% and 50% solutions of urea in DI water. After the removal of each urea solution, the sensor was rinsed with DI water to prevent urea residues from drying on the graphene layer. The results of these measurements are presented in Fig. 1: (a) Schematic of the GFET biosensor interconnected to an electronic measurement setup. The graphene sensing area between the gold electrodes is 0.9×1 mm² with lateral spacing between neighbouring sets of electrodes of 0.5 mm. (b) Measured response of graphene to DI water, 32% and 50% urea concentrations. The Fermi energy shift (the Fermi energy at zero gate voltage) was calculated from the charge neutrality point voltage determined experimentally, using an approximation of the system as a parallel-plate capacitor. The exact formula used is $\Delta E_F = \text{sgn}(-V_G) \hbar v_F \sqrt{[V_G] \pi \epsilon_0 \epsilon_r / t e}$, where V_G is the gate voltage, $\hbar$ is the reduced Planck constant, $v_F = 1 \times 10^6$ m/s is the Fermi velocity, ϵ_0 is the vacuum permittivity, $\epsilon_r = 3.9$ is the relative permittivity of SiO₂, $t = 285$ nm is the thickness of the SiO₂ layer, and e is the elementary charge.

The maximum sheet resistivity corresponds to the Fermi level passing through the charge neutrality point (CNP) of graphene. Initially, graphene is p-doped as the CNP is located at $V_G \approx 52$ V in the forward sweep. There is a pronounced hysteresis between the forward and backward gate voltage sweeps in all measurements (see Fig. SF11), which is attributed to the presence of water molecules adsorbed on graphene [26]. Furthermore, the increase in sheet resistivity of graphene between individual measurements is attributed to unintentional scratching of the graphene layer during the addition and removal of the solution droplets, which was visible under an optical microscope.

The addition of DI water causes only a small decrease in the p-doping compared to ambient air. However, the effect of urea is apparent, as higher urea concentrations cause a larger reduction in the p-doping of graphene. The 50% concentration of urea corresponds to a urea-to-water molecular ratio of 1:3 and approaches the maximum solubility of urea in water. Consequently, a lower concentration was used to prove the general trend of decreasing p-doping with increasing urea concentration. In fact, the 32% concentration was specifically chosen to be the same as the solution used in fuel additives to reduce NO_x emissions from diesel engines.

3.2. Calculations

3.2.1. Structures

Based on previous studies [13,27,28], twelve structures corresponding to five urea-to-water molecular ratios (1:0, 2:0, 1:1, 1:2, and 1:3) were calculated. Subsequently, these structures were placed on graphene, and their formation and adhesion energies were determined. The structures for each ratio differ in the position of water molecules (chain, side) and the orientation of hydrogen atoms in the water

molecule relative to graphene (H-up or H-down). All calculated structures with structural parameters are listed in Supporting information (SI). Fig. 2 provides a schematic representation of the characteristic positions and orientations of water molecules relative to the urea molecule.

Considering the charge transfer from molecules to graphene, the distance of individual atoms from the graphene surface has a significant impact, since no new chemical bonds are formed with graphene. For the selected structures, the distance from the graphene plane was evaluated for the oxygen and nitrogen atoms in urea (u_O and u_N respectively), the average height of the oxygen atoms above graphene layer in the water molecule(s) $\bar{w}_O$, the average height of the urea molecule above graphene layer $\bar{u}$, and the height of the graphene layer curvature denoted as Δ .

For all calculated ratios, u_O and u_N tend to be the highest for H-up structures. On the other hand, for H-down complexes, $\bar{u}$ and Δ are higher, and w_O is significantly higher relative to the other complexes. For a lower number of water molecules (0 or 1), when the water molecule is in the chain position (see Fig. 2a), the oxygen atom of urea is pushed down to the graphene layer. In contrast, for a higher number of water molecules (2 or 3) all heights fall between those observed for H-up and H-down.

3.2.2. Energy

The stability of the given systems was evaluated based on the adsorption (1) and formation (2) energies, where higher values correspond to more stable configurations. All calculated energies are depicted in Fig. 3 and corresponding systems in SI (Fig. SF1–SF10).

From the perspective of adsorption energy, the most stable complexes are those with the water molecule in the chain position, i.e., G1WU_chain and G2WU_asym systems. When comparing all urea-to-water molecular ratios, it can be observed that the urea molecule has the largest contribution to adsorption energy. This is due to the larger interaction surface relative to water molecules. This is followed by the water molecule in the chain position and the water molecule in the side H-up position, while the smallest contribution comes from the water molecule in the side H-down position.

When comparing formation energies, one can observe that the most stable structures are those where binding occurs in the side H-up position. The side position is naturally more stable due to two independent hydrogen bonds: one between the oxygen atom of the water molecule and the hydrogen atom of the urea molecule, and another between the hydrogen atom of the water molecule and the oxygen atom of the urea molecule. In contrast, the chain position involves bonding between the oxygen atom of the water molecule and two different hydrogen atoms of the urea molecule. The more stable H-up position (similarly to the adhesion energy results) indicates a stronger interaction between the oxygen atom of the water molecule and graphene compared to the interaction between the hydrogen atom of the water molecule and graphene in the H-down structure (Fig. 2).

3.2.3. Charge distribution

In the case of isolated urea adsorption, the oxygen atom tends to withdraw electrons from the graphene substrate, effectively acting as a p-dopant. In contrast, the hydrogen atoms in the NH₂ groups donate electrons to the graphene, contributing to n-type doping. The observed charge redistribution can be qualitatively rationalized by the differences in electronegativity with respect to carbon, with oxygen attracting electronic density and hydrogen exhibiting partial positive charge, thus donating partial negative charge. For water molecules, the doping character depends strongly on the molecular orientation relative to the graphene surface. When the hydrogen atoms of water point towards the surface, the molecule donates electrons (n-doping); when the oxygen atom faces the graphene, it withdraws electrons (p-doping).

These trends are visible in the charge density difference plots calculated for a fixed isovalue of the charge density (Fig. 4). In addition, a noticeable charge redistribution within the adsorbed molecules is

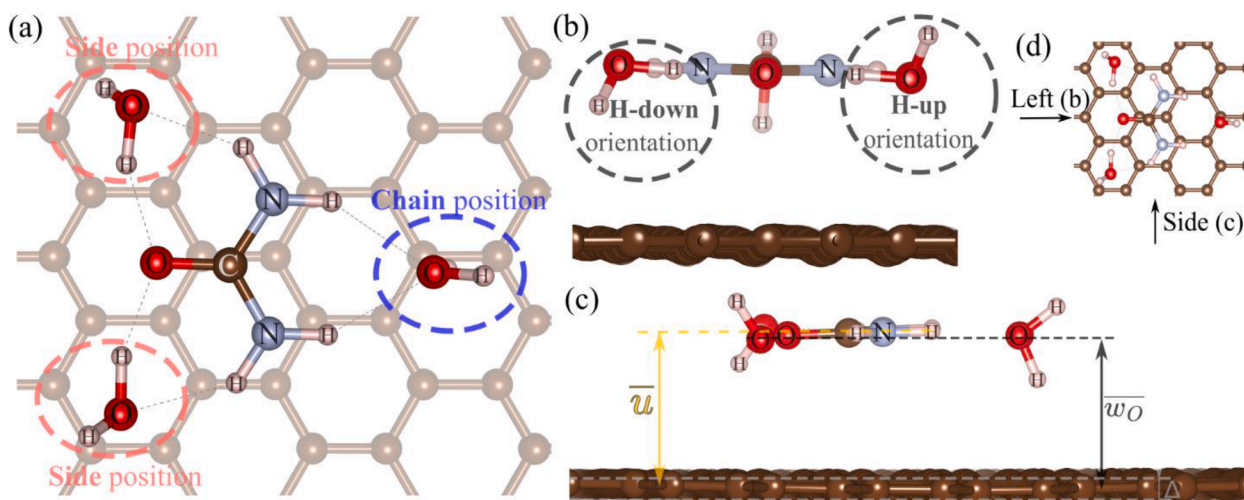


Fig. 2. Schematic representation of (a) the side and chain water position, top view, (b) H-up and H-down water molecule orientations, left view, (c) average height of urea molecule over graphene ($\bar{u}$), average height of oxygen atoms of water molecules over graphene ($\bar{w}_O$) and graphene curvature (Δ), and (d) visualisation of left and side views. Red, brown, blue, and white represents oxygen, carbon, nitrogen, and hydrogen atoms, respectively.

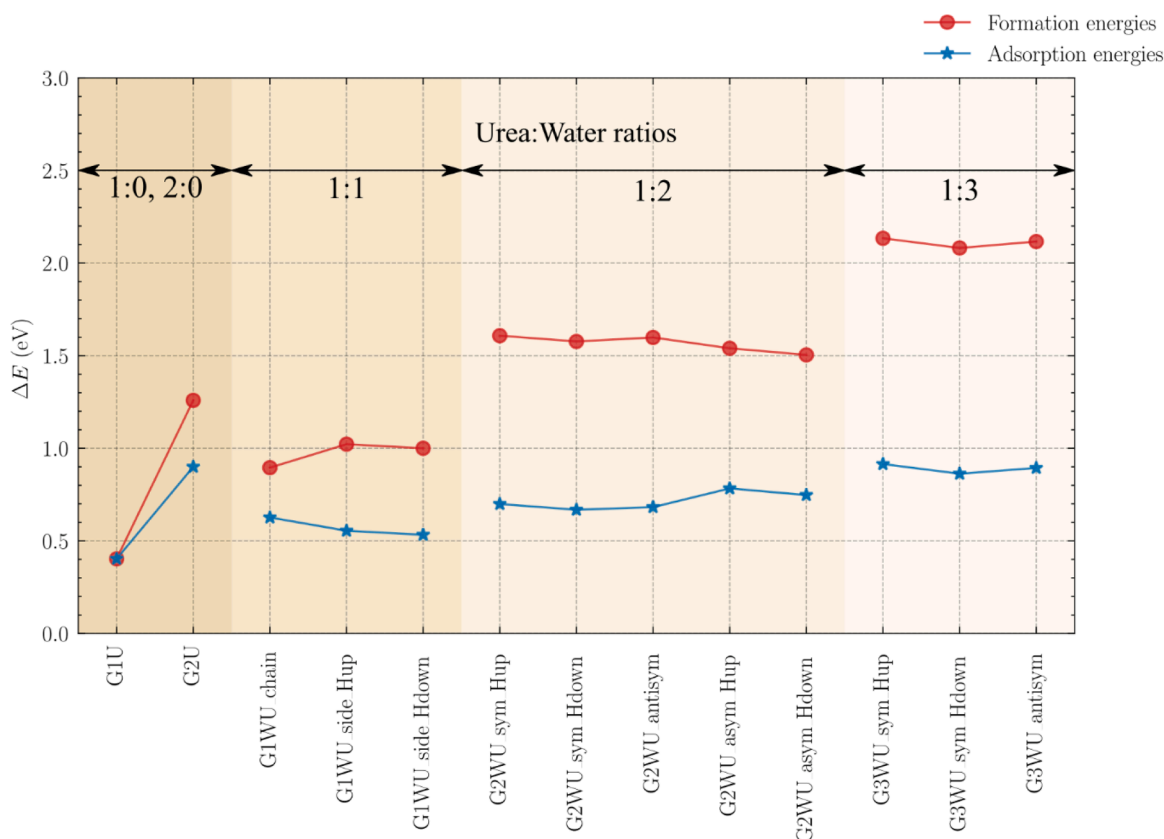


Fig. 3. Formation and adsorption energies for all calculated systems and urea-to-water molecular ratios.

observed. For example, in the case of two adsorbed urea molecules, the oxygen atom that interacts via van der Waals forces with the NH_2 groups of the neighbouring urea molecule exhibits a larger partial charge compared to an oxygen atom not involved in such intermolecular interactions (data not shown).

3.2.4. Charge redistribution

Charge redistribution was calculated using the Bader charge analysis. The results are depicted in Fig. 5. For the 1:1 ratio, the most charge

is distributed to the graphene when the water molecule is in the side position with the hydrogen orientation H-up. Almost no charge is redistributed by the H-down orientation. On the other hand, the chain position pushes charge from the graphene. This trend is consistent across all the urea-to-water molecular ratios. The average charge redistribution was also calculated based on the Boltzmann probability distribution. We can observe a descending trend in doping towards graphene with the increasing content of water.

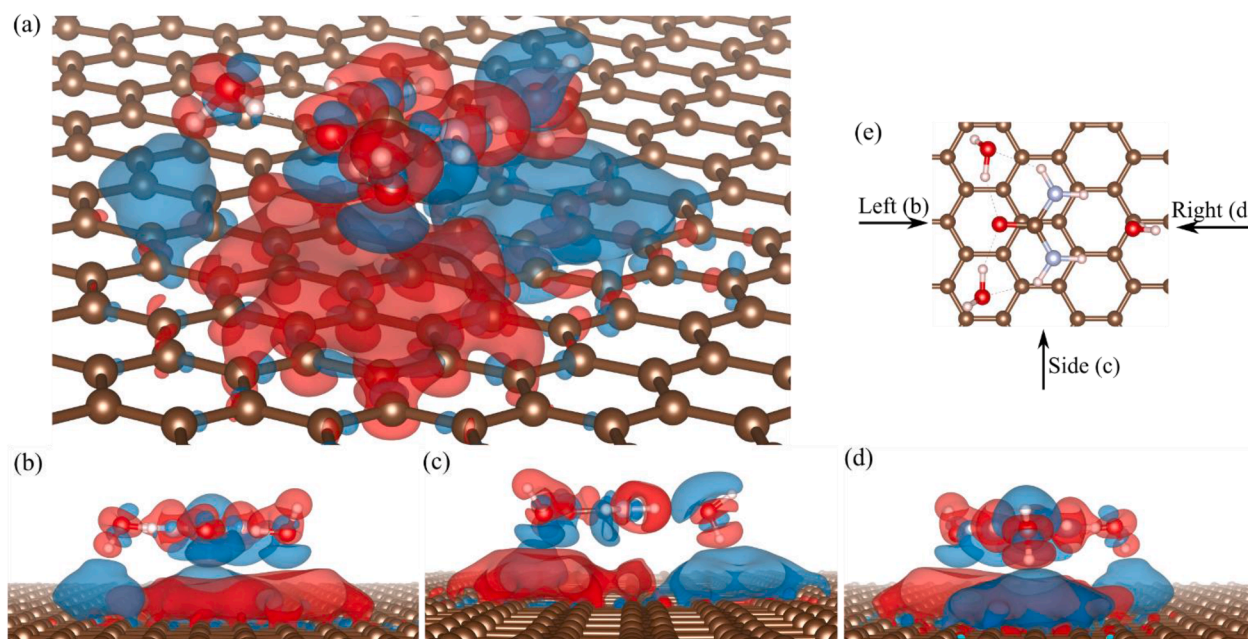


Fig. 4. Charge redistribution isosurfaces after adsorption of the G3WU_antisym structure (isosurface of density $\rho = 0.2 \text{ mC}/\text{\AA}^3$). Red indicates missing electron charge (positive charge density), blue indicates excess electron charge (negative charge density). (a) general view, (b) left (c) side and (d) right view, (e) schematic illustration of the left, side, and right views from the top perspective.

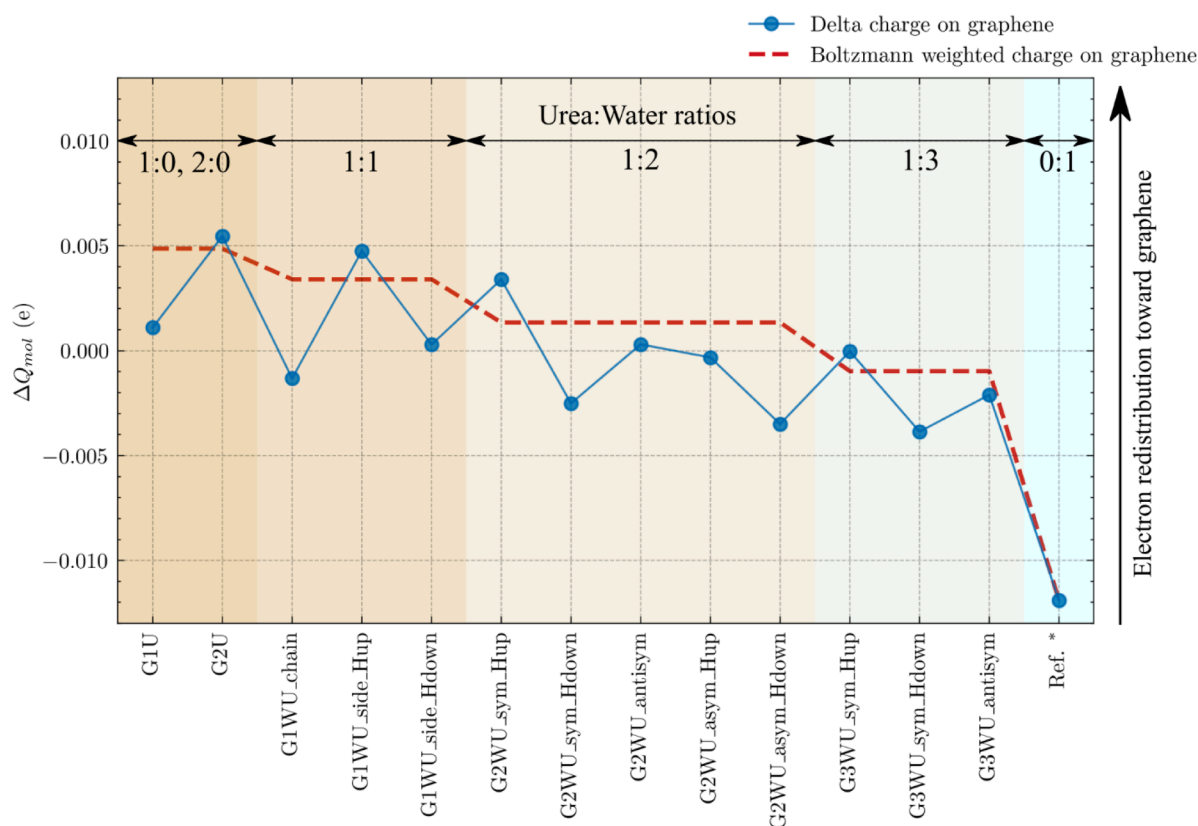


Fig. 5. Calculated charge redistribution from adsorbent to graphene using the Bader charge analyses. Ref. * adapted from [29].

3.2.5. Band structure

For all structures, the band structure was calculated with projections onto atomic orbitals of individual atoms belonging to the respective molecules and graphene. The results are presented in Fig. 6.

For all calculated band structures, no shift of the Fermi level relative

to the Dirac point was observed, indicating the absence of graphene doping. All bands corresponding to water and urea molecules are flat, suggesting that no chemical interaction takes place between graphene and the adsorbed molecules. Furthermore, these bands lie deep below the Fermi energy, which prevents which charge transfer to graphene and

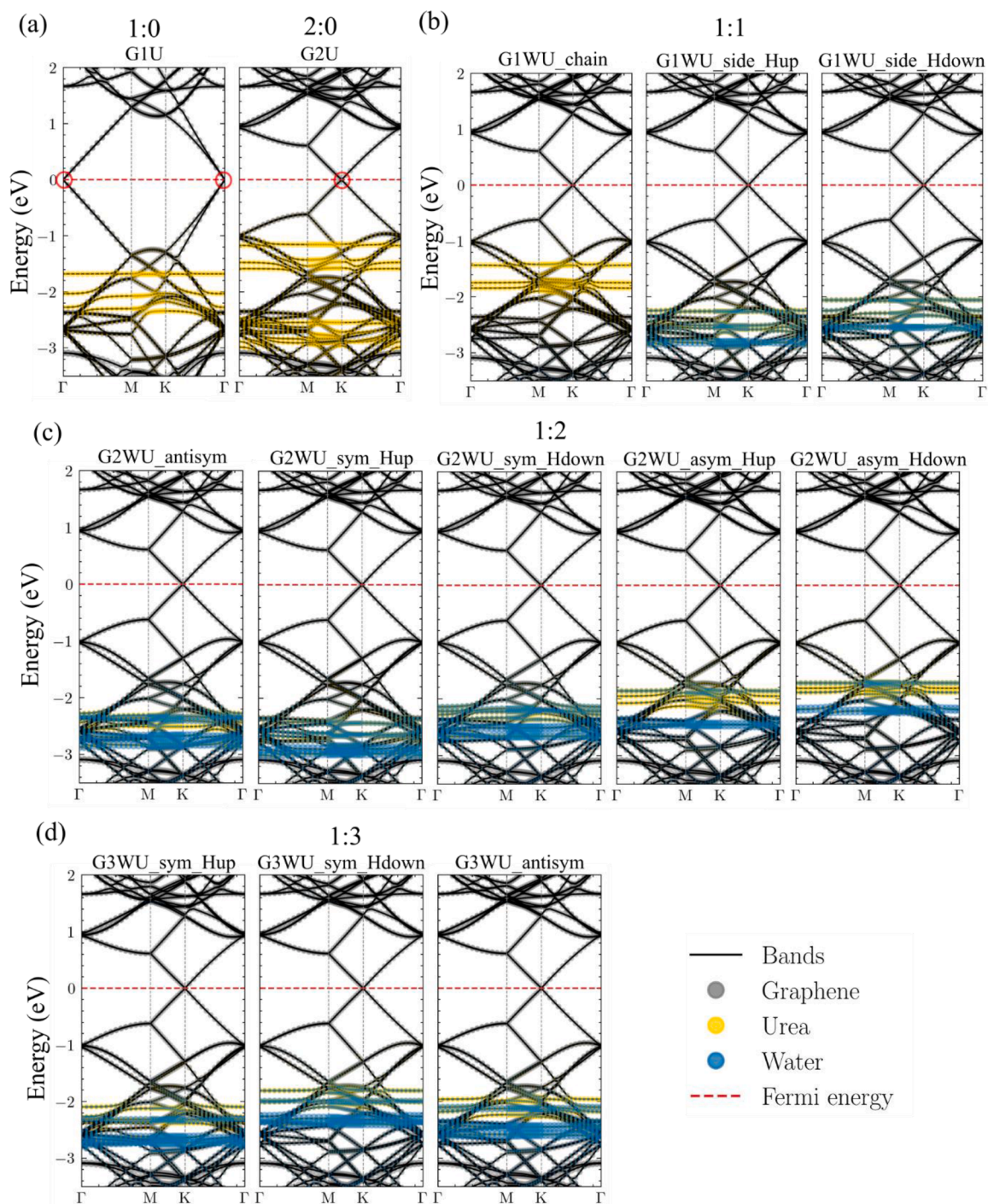


Fig. 6. Calculated folded band structures for all urea-to-water molecular ratios-with projections to the energy levels of atomic orbitals of individual molecules. (a) only urea molecule(s), Dirac points are marked by red circles, (b) urea-to-water molecular ratio 1:1, (c) urea-to-water molecular ratio 1:2 and (d) urea-to-water molecular ratio 1:3. For (b) – (d) Dirac points are at the same place as in (a) 2:0 G2U structure.

depletion of the molecular HOMO orbitals. Similarly, the LUMO orbitals (corresponding bands) are located far above the Fermi energy (not shown), precluding occupation of these empty orbitals and preventing p-doping of graphene.

Similar flat bands were observed in the article published by Nezval et al. [29] using the PBE exchange–correlation functional with the DFT+D3 dispersion correction. For water molecules oriented in the H-down direction, flat bands were observed to shift progressively from approximately 2 eV below the Fermi energy toward the Fermi energy with an increasing number of water layers. However, these bands never

crossed the Fermi energy. On the other hand, for the O-down orientation, non-flat bands were observed to cross the Fermi energy for multiple layers of water molecules, leading to p-doping of graphene. In our case, we observed similar flat bands not crossing the Fermi level for all arrangements, independent of whether the water molecules were situated in the H-down or H-up orientation. This suggests that even for a higher number of molecules, graphene would remain undoped, since no non-flat bands appear close to the Fermi energy from above. We observed bands around –2 eV, which correspond to changes in the density of states (DOS) within the energy range from –2.5 eV to –1 eV

observed by Singh and Paily [12].

From the results obtained by the Bader charge analysis, the Fermi energy shift can be estimated using the equation $\Delta E_F = \text{sgn}(-Q)\hbar v_F \sqrt{\pi|Q|/A}$, where $\hbar$ is the reduced Planck constant, v_F is the Fermi velocity of 1×10^6 m/s, Q is the transferred charge from a molecule to the graphene layer (calculated by the Bader charge analysis), and $A = 189.523 \text{ \AA}^2$ is the area of the graphene sheet (calculation supercell). From this equation, we obtain an estimated shift ranging from 64 meV to -40 meV for the 1:0 to 1:3 urea-to-water molecular ratios. However, comparing these results with the Fermi energy shift determined from the band structure calculations, we can see a discrepancy. The reason for this discrepancy is that the Bader analysis assigns charge from minima in the spatial charge distribution, which does not necessarily correspond directly to individual molecular orbitals or graphene bands. Hence, there is a spatial redistribution of charge within both graphene and the adsorbed molecules, but no charge transfer occurs between the graphene bands and the adsorbate orbitals. Consequently, there is no shift in the Fermi energy.

Singh and Paily also studied the charge transfer between the urea molecule and graphene using Mulliken population analysis [12]. They performed calculations with the SIESTA package [30,31] using the Perdew-Burke-Ernzerhof [20] exchange-correlation functional without van der Waals corrections. The charge transfer obtained in these calculations was 0.065 e from the graphene layer to the urea molecule. This would result in a shift of the Fermi level of about 160 meV, which is not observed in our calculated band structures nor in their reported DOS results.

It is important to emphasize that the presented DFT calculations correspond to static, 0 K configurations, i.e., local minima on the potential energy surface. As such, they do not include entropic contributions, thermal fluctuations, or collective effects arising in a dynamically evolving liquid environment. In reality, translational, rotational, and vibrational motion leads to a continuous distribution of molecular orientations, and adsorption/formation energies rather than a set of discrete configurations. Cooperative interactions between neighbouring molecules, including hydrogen bonding and electrostatic screening, may further modify the local interfacial environment at the graphene surface.

Therefore, the absolute value of the thermally averaged charge redistribution may differ from the static values calculated for selected structures. However, the key qualitative features, namely the absence of band hybridization and the lack of a direct Fermi level shift, are determined by the electronic structure of the graphene-adsorbate system. Therefore, although finite-temperature and collective effects may influence the magnitude of the observed doping modulation, they are not expected to alter the underlying mechanism identified in the static DFT calculations.

In relation to the experimental results, DFT calculations provide valuable insights. The simulations were performed for the main possible binding configurations of water to the urea molecule. Lower urea concentrations are therefore expected to lead either to the aggregation of urea into molecular clusters or to the formation of isolated urea molecules separated by water. In both scenarios, however, the net transferred charge appears to be negligible. This leads to a weaker p-type doping compared to graphene exposed to deionized water or ambient air conditions. Hence, at lower concentrations, doping originates from water molecules, while urea molecules do not contribute to doping. Consequently, the urea molecule acts not only as a barrier between graphene and surrounding water, preventing water from doping graphene, but also inhibits nearby water molecules from doping graphene as strongly as in the case of freely adsorbed water.

For the maximum urea solution concentration (50%, 1:3 urea-to-water molecular ratio), experimental measurements show a Fermi energy shift of nearly 70 meV (Fig. 1b). This could indicate that regions still exist on the graphene surface where graphene comes into contact exclusively with water molecules, or that the urea molecule is not

oriented parallel to the graphene plane and is surrounded by water. This scenario may correspond to a statistical distribution at room temperature, which was not considered in our DFT calculations. However, the trend predicted by the DFT calculations remains valid and manifests in the overall statistics, reflecting a reduction in the doping level of the graphene layer.

4. Conclusion

In this work, we presented the first combined experimental and DFT study of urea detection in aqueous solutions using GFET-based sensors. Experimental measurements demonstrated that an increasing urea concentration reduces the intrinsic p-doping of graphene by water, with a Fermi level shift of approximately 70 meV observed at the maximum investigated concentration (50% urea, 1:3 urea-to-water ratio). This shift indicates a significant modulation of graphene doping by urea, although residual p-doping likely persists due to incomplete surface coverage or statistical molecular orientations.

DFT simulations provided insight into the structural and electronic interactions of urea-water mixtures adsorbed on graphene. The Bader charge analysis confirmed a progressive reduction of the charge transfer to graphene with increasing water content, consistent with experimental observations. However, the band structure calculations revealed no direct Fermi level shift, suggesting that the observed experimental doping modulation arises from a spatial charge redistribution rather than a direct charge transfer between molecular orbitals and graphene bands.

The combined analysis suggests that urea molecules act as both physical and electronic barriers, preventing water-induced p-doping of graphene, while not introducing significant chemical doping themselves. This highlights the complex interplay between molecular orientation, local coverage, and thermal distribution in realistic sensor environments.

Our results clarify the doping mechanism of graphene in mixed urea-water systems and open perspectives for optimizing graphene-based sensors for high-concentration urea detection, especially in industrial applications.

Supporting Information: Additional structural parameters of individual structures, pictures of individual structures, structural parameters of structures on graphene, pictures of structures on graphene, linear combination of charge redistributions.

Data availability

Data will be made available on request. The data that support the findings of this study are at: [10.5281/zenodo.19236518](https://doi.org/10.5281/zenodo.19236518).

CRediT authorship contribution statement

O. Špaček: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **L. Supalová:** Validation, Investigation, Data curation. **J. Mach:** Validation, Supervision, Data curation. **D. Nezval:** Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **T. Šíkola:** Supervision, Funding acquisition. **M. Bartošík:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We acknowledge the support by the Grant Agency of the Czech Republic (grant No. 25-16894S), OP JAK (project No CZ.02.01.01/00/22_008/0004594 TERA FIT), and CzechNanoLab Research Infrastructure supported by MEYS CR (LM2023051).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.apsadv.2026.100978](https://doi.org/10.1016/j.apsadv.2026.100978).

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