Stability of melamine-exfoliated graphene in aqueous media: quantum-mechanical insights at the nanoscale

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In recent experiments, melamine (1,3,5-triazine-2,4,6-triamine) has been proposed as an effective exfoliating agent to obtain high quality graphene from graphite. After washing out the melamine in excess, small amounts (ppm) are still needed to stabilize the dispersion of graphene flakes in aqueous media. To understand the origin of this behaviour, we investigated the melamine-graphene-water system and the fundamental interactions that determine its structure and energetics. To disentangle the subtle interplay of hydrogen-bonding and dispersive forces we used state-of-the-art *ab initio* calculations based on density functional theory. First, we focused on the case of water molecules interacting with melamine-graphene assemblies at different melamine coverage. We found that water-melamine interactions provide the driving force for washing off the melamine from graphene. Then, we addressed the interaction of single and double layers of water molecules with the graphene surface in the presence of an adsorbed melamine molecule. We found that this melamine acts as a non-covalent anchor for keeping a number of water molecules conveniently close to the graphene surface, thus helping its stabilization in aqueous media. Our analysis helps understanding how competing weak forces can lead to a stable graphene water suspension thanks to small amounts of adsorbed melamine. From our results, we derive simple indications on how the water-graphene interfacial properties can be tuned via non-covalent adsorption of small functional molecules with H-bond donor/acceptor groups. These new hints can be helpful to prepare stable graphene dispersions in water and so to unlock graphene potential in aqueous environments.

Introduction

Carbon nanostructures and graphene-based materials are at the forefront of many technological fields, thanks to outstanding mechanical, thermal and electronic properties.¹ Graphene is already employed as constituent functional material in promising devices,² from energy storage supercapacitor³ and optoelectronics⁴ to biomedical applications.⁵ However, there are still many open scientific questions that must be addressed in order to exploit the full potential of graphene, especially in the context of soft-matter systems as living cells.⁶ A relevant example is the chemistry of graphene in water: how can we achieve and control stable dispersions of graphene nano-flakes in aqueous media? There is ongoing debate in the scientific literature on this topic:⁷ several groups have addressed graphene-water interactions with first-principles methods,⁸ and molecular simulations have been carried out to study the molecular dynamics of water (from water clusters up to water-droplets) when adsorbed on

graphene surfaces.⁹ These studies proved the expected hydrophobic nature of graphene and the non-convenient binding of water to its surface. In other terms, the water-water binding is order of magnitudes stronger than water-graphene binding: the water molecules try to maximize the H-bonds among themselves rather than interact with graphene, and even when water is squeezed between two graphene monolayers, a nano-layer 2D square ice has been predicted and experimentally detected.¹⁰

Besides these fundamental studies, several experimental routes have been developed to obtain graphene-water systems starting from graphite.¹¹ The easiest way is to prepare the graphene hydrophilic derivative, graphene oxide, by oxidative exfoliation of graphite.¹² But, the formation of covalent C-O bonds alters the C sp² honeycomb lattice, with a significant worsening of overall electronic properties.¹³ Other approaches have considered sonication of graphite in presence of ionic surfactants,¹⁴ pyrene derivatives,¹⁵ or polymers.¹⁶ Several theoretical simulations have proven that these systems cover most of the graphene surface, leaving only small available regions for further interactions.¹⁷

Recently, some of us have proposed an effective approach to obtain high quality graphene from graphite with melamine (1,3,5-triazine-2,4,6-triamine) as non-covalent exfoliating agent.¹⁸ After ball-milling graphite and melamine, the exfoliated graphene layers can be dispersed in organic solvents (such as DMF) or in aqueous solution. In particular, melamine can be

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easily washed out with water, leaving stable graphene aqueous dispersions. However, elemental analysis of these samples always showed the presence of small melamine amounts (ppm), and further washing led to graphene precipitation. From these experiments it clearly appears that melamine plays a crucial role in stabilizing the graphene dispersion in water. The origin and molecular bases of such behaviour are still unclear, as well as the fundamental nature and the structural features of the enduring graphene-melamine-water interactions. Here, we address these issues with state-of-the-art first-principles calculations: *ab initio* methods provide the best means to dissect and rationalize all the forces into play with an atomistic perspective and with no empirical bias.

We focused on how water molecules interact with just-exfoliated melamine-graphene layers and how melamine molecules tune the adsorption of full water layers on graphene. In this way, we analysed the graphene-melamine-water three-body system in two crucial processes: washing of excess melamine after ball-milling exfoliation, and stabilization of graphene aqueous dispersion. Besides providing explanations to experimental observations, our results can be instrumental to the rational design of melamine-alternative non-toxic molecules for the effective dispersion of graphene flakes in solution.

Methods and computational details

We have characterized the structural and electronic features of the melamine/water/graphene systems by periodic-spin-polarized density functional theory (DFT)¹⁹ calculations as implemented in the VASP code (version 5.3.5).²⁰ We used the Perdew-Burke-Ernzerhof (PBE)²¹ functional and the standard projector augmented wave (PAW) potentials.²² A kinetic energy cut-off of 750 eV was used to convert plane wave basis set for all the calculations. The stopping criterion for the convergence of the forces was always < 0.03 eV/Å on all atoms. Each surface slab was modelled with a vacuum space of 15 Å, and the asymmetry was corrected with a dipole correction introduced in the vacuum gap.²³ We used a $21 \times 21 \times 1$ *k*-point sampling based on the gamma centred Monkhorst-Pack mesh for the graphene unit cell, and different divisions were used according to the size of the super-cell structures used to study different melamine/water coverage. In all the calculations the Brillouin zone was integrated with the Gaussian smearing method (0.05 eV as smearing width), while projected densities of states (DOS) were all computed with the tetrahedral smearing method including Bloch's correction.

Van der Waals forces play an important role in determining the structure and energetics of extended carbon-based nanomaterials.²⁴ Approximate DFT density functional are unable to correctly describe these weak intermolecular interactions,²⁵ and several efforts are being devoted to solve this DFT flaw with diverse strategies.²⁶ Here, we exploited the Dispersion-corrected DFT scheme, proposed by Grimme,²⁷ where these weak interactions are described as an additional atom-based pairwise dispersion energy term. This approach achieves a correct description of the long-range interactions

between molecules and graphene-like structures with no additional computational cost. In particular, we used the most recent of Grimme's approaches (DFT-D3), with the Becke-Johnson damping function (BJ),²⁸ as implemented in VASP.

Particular care should be taken in choosing the appropriate dispersion corrected DFT scheme. For example, it is well known that DFT-D based approaches can be inaccurate for describing transition metals and molecule-metal interactions.²⁹ Our choice of PBE-D3 (with BJ damping) for studying graphene-melamine-water systems responds, however, to its suitability for related systems reported in recent literature. Van Troeye et al.³⁰ have compared van der Waals density functionals and different DFT-D based approaches to study the structural and vibrational features of graphite and they found a very good agreement ($\sim 1\%$ error) between PBE-D3 and experimental lattice constants and cohesive energy (see Table II in Ref. 30). Grimme and co-workers³¹ have recently tested the DFT-D approaches on the structures and lattice energies for several ice polymorphs and they found that PBE-D3 provides good results with a mean absolute relative error on predicted structures around 3% and a mean absolute deviation on lattice energies around 2 kcal/mol against experimental benchmarks.

On these bases, we can safely consider our results qualitatively reliable and for these same reasons DFT-D3 has been extensively applied to study molecular absorption on graphene and related systems.³²

Results and discussion

Recent studies on melamine and graphene/graphite finite-size models have proven that exfoliation of graphene from graphite occurs via the formation of strong H-bond networks among adsorbed exfoliating molecules.¹⁸ Experimental studies addressing adsorption of melamine on coinage metal hexagonal surfaces have proven that melamine molecules can form large 2D supra-molecular assemblies that follow the hexagonal pattern of the substrate.³³ On these bases, we investigated melamine adsorption on graphene starting from a single adsorbed molecule (CM0) to more complex 2D melamine networks at increasing area coverages with trigonal (CM1), hexagonal (CM2) and tetragonal (CM3) patterns, as depicted by Figure 1. Similar 2D melamine assemblies have been also observed with STM on highly oriented pyrolytic graphite.³⁴ For these systems, the total adsorption energies ($E_{ads-CMx}$) are computed as:

$$E_{ads-CMx} = E_{G-CMx} - (n \cdot E_G) - (m \cdot E_M) \quad (x = 0, 1, 2, 3) \quad (\text{eq. 1})$$

where E_{G-CMx} , E_G , and E_M are the total energies of the total systems, the isolated graphene and the isolated melamine molecule, respectively. The n and m indexes are the number of graphene unit cells in the total system and the number of adsorbed melamine molecules, respectively.

Fig. 1 Lateral and top views of supra-molecular 2D melamine networks on graphene: isolated melamine molecule (CM0), trigonal (CM1), hexagonal (CM2) and tetragonal (CM3) patterns. Graphene is omitted in the top views for clarity. Color legend: light green spheres represent the C atoms of graphene, green spheres the C atoms of melamine, cyan and white spheres represent N and H atoms, respectively; dashed lines represent the unit-cell replicated in our periodic calculations; cartoons of green triangles represent the 2D arrangements of melamine molecules.

The total adsorption energies have been decomposed further in three main contributions:

$$E_{\text{ads-CMx}} = E_{G-M} + E_{G\text{-dist}} + E_{M-M} = (E_{G\text{-CMx}} - E_{G^*} - E_{\text{CMx}}) + (E_{G^*} - n \cdot E_G) + (E_{\text{CMx}} - m \cdot E_M) \quad (\text{eq. 2})$$

where E_{G^*} and E_{CMx} are the total energies of the graphene layer and the 2D melamine assembly, respectively, taken from the G-CMx total system equilibrium structure. From this analysis we determine the direct interaction energy between the total melamine layer and graphene (E_{G-M}), the distortion energy of graphene from its unperturbed equilibrium structure ($E_{G\text{-dist}}$) and the cohesive energy of the melamine supra-molecular network (E_{M-M}). Figure 2 shows these terms together with the total adsorption energy ($E_{\text{ads-CMx}}$).

At increasing coverage, interaction energy E_{G-M} and cohesive energy E_{M-M} become both more negative with the same order of magnitude, contributing equally to the overall adsorption energy. The slight increase of E_{G-M} when going from CM0 to CM1 is due to the peculiar CM1 minimum-energy structure: the isolated melamine (CM0) maximizes the interaction with graphene by orienting its -NH_2 moieties toward the aromatic surfaces (distance between melamine and graphene surface is ~ 3.2 Å); when melamine-melamine interactions come into play, the -NH_2 groups are no longer directed towards the graphene surface, weakening the melamine-graphene interaction and resulting in a distorted network with an average distance between melamine molecules and graphene of ~ 3.5 Å in CM1, as depicted by Figure S1 in Supporting Information (SI).

Fig. 2 Adsorption energies (E_{ads}) and energy-decomposition terms from eq. 2 and eq. 4 for the CMx (full lines) and CMxW (dashed lines) systems.

On the contrary, the melamine adsorption at increasing coverage does not affect the planar structure of graphene. Distortion energies $E_{G\text{-dist}}$ in Figure 2 are close to zero in all cases and, consequently, the graphene electronic structure retains the main features as in its isolated form, as shown by Figure S2 in SI. This result explains why the non-covalent exfoliation with melamine does not spoil the peculiar electronic features of graphene.

When washing with water the exfoliated graphene flakes after ball milling, the solvent molecules interact first with the melamine layer that is covering the graphene surface. We addressed this interaction in our study by considering the insertion of few water molecules in the “hollows” that are present in CM1 and CM2 melamine supra-molecular patterns. Experimental evidence indicates the possible formation of convenient H-bonds between water and the available melamine -NH_2 groups. Figure 3 displays the equilibrium structures for CM1 with 2 water molecules and CM2 with 4 water molecules.

The corresponding energetics has been analysed as in eq. 1 and eq. 2 by considering the total adsorption energies and the different contributions defined as:

$$E_{\text{ads-CMxW}} = E_{G\text{-CMxW}} - n \cdot E_G - m \cdot E_M - b \cdot E_W \quad (x = 1, 2; b = 1, 2) \quad (\text{eq. 3})$$

$$E_{\text{ads-CMxW}} = E_{G-MW} + E_{G\text{-dist}} + E_{M-MW} = (E_{G\text{-CMxW}} - E_{G^*} - E_{\text{CMxW}}) + (E_{G^*} - n \cdot E_G) + (E_{\text{CMxW}} - m \cdot E_M - b \cdot E_W) \quad (\text{eq. 4})$$

where $E_{G\text{-CMxW}}$ is the total energy of each given graphene-melamine-water structure, and E_W is that of an isolated water molecule, and b is the total number of water molecules in the total system. The direct interaction energy between the whole melamine-water layer and graphene is quantified by E_{G-MW} , and E_{M-MW} represents the internal cohesive energy of the melamine-water supra-molecular network; Figure 2 depicts all these terms.

Figure 3. Minimum-energy geometries for the CMx-W systems: CM1+2H₂O and CM2+4H₂O; the insets collect the distances (in Å) for the H-bonds (highlighted by dotted lines).

Also in presence of water molecules, graphene distortion energies (solid and dashed red lines) are negligible, *i.e.* very close to 0 eV. The solid (E_{G-M}) and dashed (E_{G-MW}) green lines overlap, which means that including water in the adsorbed layer is not changing the direct interaction energy between the adsorbate (melamine-water) and the substrate (graphene). This result is in agreement with recent literature that reports water and graphene to interact only through very weak dispersive forces.⁸⁻⁹ On the contrary, there is a great change in the overall adsorption energy (black line in Figure 2) upon inclusion of water, due to the improved cohesive energies coming from the favorable melamine-water intra-layer interactions (E_{M-MW} , dashed blue line). In CM1-2H₂O system, our PBE-D3 calculations predicted the formation of one water-water H-bond, and the water molecules are involved in three and two H-bonds with melamine -NH₂ groups and aromatic N species, as depicted by Figure 3 together with inter-atomic distances. Overall, there are six new H-bonds that are responsible for the extra stabilization of the adsorbed layer equal to ~ -0.22 eV per H-bond. In the case of CM2-4H₂O, there are 4 water-water H-bonds and each water molecule is involved in two H-bonds with the closest melamine molecules, as depicted by Figure 3. In this case there are a total of 12 H-bonds in the adsorbed supra-molecular network and the average energy for each of them is ~ -0.24 eV per H-bond. Moreover, considering the full coverage of an infinite 2D graphene layer, the normalized adsorption energies are -0.09, -0.10 and -0.12 eV per graphene formula unit for CM1, CM2 and CM3, respectively. Considering the inclusion of water these values go to -0.22 and -0.24 eV per graphene formula unit for CM1-2H₂O and CM2-4H₂O, respectively. In other words, the formation of favourable melamine-water H-bonds represents a thermodynamic driving force for displacing the most compact melamine network (CM3) toward more loose supra-molecular patterns (CM1 and CM2) that are able to accommodate water molecules. Once these molecules are included into the first adsorbate layer the solvent can easily interact with the graphene-melamine-water system.

We must point out that our calculations provide insights on the very initial stage of the washing process. We have estimated the relative stability of different melamine coverage on graphene in

presence of water molecules. Our model neglects important contributions from molecular vibrations and configurational entropy, but the computed energy trend proves the role of water-melamine interactions as driving force for loosening the compact melamine layer and for including water molecules in the first adsorbed monolayer. For a more detailed description of the next steps along the washing process, molecular dynamics (MD) simulations are needed: MD would provide important details on the effects of temperature and nuclear motions in the displacement of melamine molecules from the compact supra-molecular layer.

The repeated washing procedures result in graphene water dispersion, but melamine is still present in ppm on the graphene surface. Without this tiny amount of melamine, graphene would not be stable in aqueous medium and would precipitate. To model the graphene-melamine-water system in a water-rich environment, we started from pure water adsorbed layers. An extensive study of all the possible configurations of liquid water on graphene is beyond our purpose and has already been addressed in recent literature.⁹ Here, we aim at understanding how a single adsorbed melamine molecule affects the interaction between graphene and water. Thus, we have chosen only two possible very different layers of water molecules, CW1 and CW2. The structure of these water layers on graphene have been inspired by recent work on water adsorption and dynamics on graphene and on noble-metal hexagonal surfaces.³⁵ We performed structural optimizations of these water layers on the plain graphene surface. The relaxed systems retain their starting “ice-like” geometries, which are depicted by Figure S3 in SI together with their main structural parameters. Then we inserted the melamine molecule on the graphene surface (removing 3 and 4 water molecules in CW1 and CW2, respectively). Figure 4 depicts the relative relaxed structures CW1-M and CW2-M.

First, we must note that the presence of water is not altering the melamine-graphene interaction. Considering the adsorption energies of the isolated melamine defined as in eq.1 for $x=0$, but at the equilibrium geometries of CW1-M and CW2-M systems, we found values of -0.56 and -0.58 eV, respectively, which are unchanged from the CM0 case (-0.56 eV) reported in Figure 2.

From the optimized geometries of the two CW1-M and CW2-M configurations of the graphene-melamine-water system we can easily identify the water molecules that interact directly with melamine via H-bonding, even by considering the simple geometrical parameters that have been extensively used to describe H-bond interactions in water (see Figure 4). With this definition, we found in the first solvation shells (W1) a total number of 7 and 9 water molecules that are H-bonded to the melamine in CW1-M and CW2-M, respectively.

Figure 4. Minimum energy structures of the CW1-M and CW2-M systems; bottom panel reports the structural parameters to define an H-bond with respect to the relative position of H atom and the h-bonding donor (D) and acceptor (A); the cartoon representation of the CWn-M systems with the division of water molecules between the first-solvation shell (W1) and the other water molecules (WN).

The average H-bonding energies in these two configurations have been evaluated as follow:

$$E_{HB}(M-W1) = (E_{MW1} - E_M - E_{W1}) / n_{W1} \quad (eq. 5)$$

where E_{MW1} , E_M and E_{W1} are the total energy of the MW1 monolayer, the melamine molecule and the W1 supramolecular layer, respectively, and n_{W1} represents the number of 7 and 9 water molecules in CW1-M and CW2-M configurations. Table 1 lists the average H-bonding energies and the corresponding average H-bond structural parameters.

Table 1. Structural features and energies for the H-bonds in CWx-M systems. Energies (E_{HB} M-W1) are normalized with respect of H-bonded water molecules (n_{W1}); distances are in angstroms (Å) and angles in degrees (°).

	CW1-M	CW2-M
O-H...N (Å)	1.8 ± 0.2	1.7 ± 0.02
N-H...O (Å)	1.9 ± 0.2	1.9 ± 0.1
ONH (°)	15.1 ± 5.9	34.2 ± 1.6
NOH (°)	6.3 ± 0.8	3.3 ± 1.7
n_{W1} (n° interact.)	7	9
E_{HB} M-W1 (eV/wm)	-0.14	-0.28

Melamine-water interaction on graphene is strongly dependent of the solvent configuration; in CW1-M there are only 7 H-bonds with interaction distances varying from 1.6 to 2.0 Å when water is the H-bond donor and from 1.7 to 2.1 when the melamine is the donor. The final minimum-energy CW1-M structure shows that the water molecules in this configuration are not disrupting

the water-water bi-layer supra-molecular structure to optimize the melamine-water interactions. In CW2-M instead, the minimum-energy structure displays a strong change in the water layer organization and all the possible melamine-water H-bonding interactions are exploited in this system, with a total number of 9 H-bonds and average structural features with less variations than in the CW1-M case. These features explain the difference in the average H-bonding energies in the two configurations. Noteworthy, the computed average E_{HB} for each H-bonded water molecule goes from -0.14 eV in CW1-M to -0.28 eV in CW2-M (-3.2 and -6.5 kcal·mol⁻¹, respectively), a value range that can account for the breaking of a water-water H-bond (~ -0.2 eV / ~ -4.5 kcal·mol⁻¹)³⁶ and the convenient formation of a melamine-water H-bond. In other words, the melamine acts as an anchor on the graphene surface and interacts with convenient H-bonds with the solvent molecules in the first water layer, keeping the graphene stable in the aqueous dispersion.

Conclusions

In this work, we presented state-of-the-art first-principles calculations on the graphene-melamine-water system and we performed an in-depth analysis on the undergoing interactions that determine its structure and overall stability.

In the melamine-rich case, we found different possible supra-molecular patterns of favourably adsorbed melamine molecules on graphene. We proved that the interaction with these melamine molecules does not compromise the graphene excellent electronic properties. The introduction of few water molecules within the melamine networks changed the relative stabilities of the 2D supra-molecular assemblies, leading to less compact melamine layer and to the formation of convenient melamine-water H-bonds. The result is a stable melamine-water heteromolecular array³⁷ that can easily interact with other solvent molecules. This explains the very initial stage of the washing process: adsorption of compact melamine layers is mandatory to exfoliate graphite, but the interaction with just few water molecules helps the 2D melamine network to loosen up.

On the other hand, we investigated the adsorption of mono- and bi-layers of water molecules on graphene in presence of an adsorbed melamine molecule. We found that melamine -NH₂ groups and N atoms in the aromatic ring can be both involved in convenient H-bonds with water molecules. The computed energetics for these bonds can justify the breaking of a water-water H-bond and the formation of a melamine-water H-bond. At the same time, these water-melamine interactions did not affect the convenient adsorption of melamine to graphene. In other words, our study proves that the melamine molecule is acting as a van der Waals anchor that keeps a number of water molecules conveniently bound via H-bonds.

In summary, our results provided a better understanding and a quantitative estimate of the non-covalent interactions, namely dispersion and hydrogen-bonding, that provide the necessary thermodynamic driving force to stabilize the graphene-water systems with small amount of melamine. In perspective, our

analysis suggests a design strategy for obtaining stable pristine graphene aqueous dispersions: use of small functional molecules that can anchor effectively on the graphene, but at the same time can form convenient H-bonds with water molecules. Our laboratories are pursuing this direction to find non-toxic alternatives to melamine for preparing stable graphene aqueous dispersion to better study the role of non-modified graphene in biomedical applications.

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ARTICLE

SUPPORTING INFORMATION

Melamine-exfoliated graphene aqueous dispersion: unveiling microsolvation features with density functional theoryAntonio M. Rodríguez,^a Ana B. Muñoz-García,^a Orlando Crescenzi,^a Ester Vásquez,^b and Michele Pavone^a^a Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Comp. Univ. Monte Sant'Angelo Via Cintia 21, 80126 Naples, Italy.^b Departamento de Química Orgánica, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain. **Figure S1.** Side view of the minimum-energy CMx geometries obtained at the PBE-D3 level of theory.

Figure S2. Partial densities of states (PDOS) at the PBE level of theory for the CM_x systems. For visualization purposes, only C (p orbitals) contributions are shown for graphene and the melamine contributions are shown as the sum of the C-N-H orbitals.

Figure S3. Geometries and structural features for the CW_x systems. In all cases, distances are in angstroms.

Graphical Table of Content

First-principles calculations reveal the roles of melamine-water H-bond and melamine-graphene interaction in the stability of melamine-exfoliated graphene aqueous dispersions.