Supporting Information

Graphene Oxide as a Pb(II) Separation Medium: Has Part of the Story Been Overlooked?
Manh-Thuong Nguyen, Jun Zhang, Venkateshkumar Prabhakaran, Shuai Tan, Eric T. Baxter, Vaithiyalingam Shutthanandan, Grant E. Johnson*, Roger Rousseau, and Vassiliki-Alexandra Glezakou*

Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA, USA

Vanda.Glezakou@pnnl.gov; Grant.Johnson@pnnl.gov
Figure S1. (a, b) Graphene functionalization: two different coverages of hydroxyl groups. The same for other functional groups. High and low coverage corresponds to 0.125 and 0.06 monolayer coverage of functional groups, respectively. (c) The 2D unit cell of 1 PbCl₂ and 180 water molecules on graphene-COOH (high coverage). Color code: O (red), C (grey), H (white, small sphere), Cl (green), Pb (dark yellow, large sphere).

Table S1. Electrostatic potential fitting charges (unit |e|) of functional groups at the low coverage.

|        | OH          | O            | COOH         |
|--------|-------------|--------------|--------------|
| H      | -0.64(O) /  | -0.33        | +0.23(C)/-0.41(O)/ |
|        | +0.35(H)    |              | -0.50(O)/+0.42(H) |

Table S1 summarizes the charges on the functional group atoms to emphasize the difference in adsorption capacity of OH and COOH compared to H and O.
S2. Potential of the mean force

The potential of mean force (PMF) is given by $W(z) = -k_B T \ln \left( \frac{\rho(z)}{\rho({\text{bulk}})} \right)$, in which $\rho({\text{bulk}})$ is the water density in the bulk and is approximately unity.

On pristine graphene, the first density peak corresponds to the first minimum in the PMF, Fig. 1(a) and Fig. S2(a). To move from the first water layer to the second one a water molecule needs to surpass a free energy barrier of about 45 meV.

Figure S2. The potential of mean force calculated from the water density (see the Method section) with different functional groups at low and high coverages.

On H-graphene, the free energy barrier for a water molecule to escape from the first layer to the second one is, about 40 meV, Fig S2(b).
The free energy barrier for water in the first layer to move to the second layer in the low OH coverage case is as high as 60 meV, and at high OH coverage, it is 45 meV, Fig. S2(c). Notably, the PMFs show a significant difference between the low and high O coverage cases, namely, the free energy barrier for molecules to move from the first to the second water layer is about 45 meV (high O coverage) and 25 meV (low O coverage), Fig. S2(d).

On HOOC-graphene the free energy depth of the well corresponding to the first peak is about 40 meV. At low –COOH coverage, the first and the second water density peaks have almost the same height. The free energy surface along the z direction in this case is flatter than other cases, with the highest free energy barrier for water to escape from the first peak is just about 20 meV, Fig. S2(e).

**S3. Coordination number**

![Figure S3. Distribution of water coordination number in the first layer.](image)

Closely related to the density of water in the first layer is the water coordination number (CN) – the number of water molecules surrounding a water in the first solvation cell. Fig. S3 shows the variation of this parameter and how the water molecules are distributed with...
respect to the CN. Implicit in this parameter are the effects of the surface-water interactions. The pristine, H- and O-functionalized graphene, Fig. S3(a), S3(b) and S3(d), show similar trends especially for the higher coverages (blue), where 60-70% of the waters have CN of ~3. Lower coverages (H and O, red) lead to a lower CN, potentially due to a more corrugated surface that disrupts the water coordination environment. The opposite effect is observed for the OH and COOH groups, Fig. S3(c) and S3(e), where for the low coverages (red) about 40-50% of the waters exhibit a CN of ~2, while for the higher coverage, about 40% of the waters exhibit a CN of ~1. An interesting observation is that for the last two more hydrophilic groups, we observe a small population of waters with CN equal to 0, implying that all waters are essentially interacting with the functional groups.

S4. Orientation of water molecules
Structural properties of water at a solid interface are always of uttermost importance as they can provide details on how water interacts with the surface. We describe the relative orientation of water with respect to the underlying surface, with the following parameters: (i) the angle between the surface normal and the dipole moment vector of a water molecule $\theta$, and (ii) the angle between the surface normal and the molecular plane normal of a water molecule $\omega$. Fig. S4 shows the distribution of the two parameters in the different systems. On the pristine graphene surface, the distribution function of $\theta$ is rather broad and somewhat symmetric about the most probable value of 90$^\circ$, Fig. S4(a). Consistent with results reported previously, the molecular dipoles fluctuate around the 90$^\circ$ value, meaning they can be parallel or anti-parallel to surface normal, but we see a large deviations from the central value. At the same time, there is no water molecule with $\omega$ equal to 0, Fig. S4(b), means that no water plane is completely perpendicular to the surface. The wide range of distribution over both $\theta$ and $\omega$ also implies that the rotation barrier of water is rather small, facilitating the 2D diffusion on the surface. With O-graphene, we found that the distribution of $\theta$ becomes more localized. At low O-coverage, there are more water
molecules with molecular dipole moments nearly parallel to the surface, Fig. S4(c). Additionally, the angle $\omega$ of $45^\circ$ also become more favorable, Fig. S4(d). At low O coverage, distribution function at $\theta$ of $60^\circ$ is becomes dominant, nevertheless, the distribution function of $\omega$ is similar to the one in the case of pristine graphene. With H-Gr, at both low and high H coverage, the distribution function of $\theta$ becomes more localized compared to that in the case of pristine graphene, Fig. S4(e). More notably, molecular plane of water is getting more and more perpendicular to the surface, Fig. S4(f). With OH-graphene, while 0.06 OH-coverage doesn’t show significant effects on the distributions of $\theta$ and $\omega$, 0.12 OH-coverage remarkably changes these distributions, Fig. S4(g-h). The clearly localized peak at $95^\circ$, Fig. S4(g), indicates more water molecules dipole moment nearly parallel to the surface, at the same time, the distribution of $\omega$ also suggests more water molecules align their molecular plane perpendicular to the surface. Finally, with COOH-graphene, at low COOH-coverage molecules with $\theta$ of $120^\circ$ become dominant in number, Fig. S4(i), showing opposite trend with 0.06 O-coverage. And different with most cases, here, molecules with $\omega$ of $40^\circ$ are more abundant, Fig. S4(j). At high COOH-coverage, there are two clear orientations for the dipole moment, one at $\theta$ of $60^\circ$ and one at $\theta$ of $150^\circ$, Fig. S4(i). Water molecules with molecular plane perpendicular to the surface also occupy a major portion.
**Figure S4.** Orientation distribution function of water molecules in the first interfacial layer, at different coverage of functional groups. θ is the angle between water dipole moment and the surface normal, ω is the angle between molecular plane of water and the surface normal. (0.12 = high coverage, 0.06 = low coverage)

**S5. Water transport in the first layer**

Having learned about the water distribution above functionalized graphene surfaces, we now look at the 2D diffusion coefficient of water in the first layer. We computed the diffusion coefficients of water in the first interfacial layer as:

$$D = \lim_{\tau \to \infty} \frac{\langle (r(t + \tau) - r(t))^2 \rangle}{2d t C_{xy}(\tau)}$$

in which $d$ is 1, 2 and for 1-, 2- dimensional (1D and 2D) diffusion, respectively, and $C_{xy}$ is the continuous survival function of water molecule in the first layer. From a 45-ps trajectory
for each system, we extracted 15 3-ps intervals to compute D when only molecules continuously remaining in the first layer within such an interval are selected. One should keep in mind that with the choice of the limit of $\tau$ is non-trivial and the diffusion coefficient can be highly sensitive to the choice of $\tau$. Here, to first approximation and for the purpose of studying the influence of functional groups, we adopted the limit of 3 ps for $\tau$. The diffusion coefficients were averaged over the 15 intervals.

In Table S2 we list the x-y (parallel to the surface, $D_\parallel$) and z (perpendicular to the surface, $D_\perp$) components of diffusion coefficients. For 2D diffusion, in the case of pristine $D_\parallel$ is $2.1 \times 10^{-5}$ cm$^2$/s. The low coverage of the functional groups O or COOH does not really change $D_{xy}$, while with OH $D_\parallel$ decreases to $1.8 \times 10^{-5}$ cm$^2$/s, and with H, $D_\parallel$ increases to $2.3 \times 10^{-5}$ cm$^2$/s. At high functional coverage, $D_\parallel$ in all cases decreases, down to less than $1.9 \times 10^{-5}$ cm$^2$/s.

The diffusion coefficient along the z direction, $D_\perp$, also clearly changed by functionalization. We did not find any significant change of $D_\perp$ with respect to functional groups except for OH and COOH. High OH or COOH coverage leads to lower $D_\perp$ with respective to $D_\perp$ (pristine).

We found that compared to the diffusion coefficient of bulk water (computed at $1.9 \times 10^{-5}$ cm$^2$/s), water in the interfacial layers diffuses slightly faster. This is consistent with previous study by Gordillo and Marti.4

**Table S2.** Diffusion coefficients ($10^{-5}$ cm$^2$/s) of water in the first interfacial layer. $D_\parallel$: x-y diffusion coefficient, $Dx$: x-diffusion coefficient, $Dy$: y-diffusion coefficient, $D_\perp$: z-diffusion coefficient.

|       | Gr (0.12) | O (0.06) | O (0.12) | H (0.12) | H (0.06) | OH (0.12) | OH (0.06) | COOH (0.12) | COOH (0.06) |
|-------|-----------|----------|----------|----------|----------|-----------|-----------|-------------|-------------|
| $D_\parallel$ | 2.1       | 1.8      | 2.1      | 1.9      | 2.3      | 1.6       | 1.8       | 1.8         | 2.1         |
| $Dx$   | 2.0       | 1.7      | 2.1      | 1.9      | 2.3      | 1.7       | 1.7       | 1.7         | 2.3         |
| $Dy$   | 2.1       | 2.0      | 2.1      | 1.9      | 2.3      | 1.6       | 1.8       | 1.8         | 2.2         |
| $D_\perp$ | 2.1       | 2.1      | 2.1      | 2.2      | 2.0      | 1.5       | 1.8       | 1.2         | 2.2         |
| Average | 2.1       | 1.9      | 2.1      | 2.0      | 2.2      | 1.6       | 1.8       | 1.6         | 2.2         |
We estimate characteristic times for the adsorption and rotation of water molecules in the first layer, considering the correlation functions

\[ C_2(\tau) = \frac{\langle h(\tau)h(0) \rangle}{\langle h(0)h(0) \rangle} \]

\[ C_\theta(\tau) = \frac{\langle \theta(\tau)\theta(0) \rangle}{\langle \theta(0)\theta(0) \rangle} \]

in which \( h \) is 1 if a water molecule is in the first layer and 0 otherwise, \( \theta \) is the angle between the dipole moment of a water molecule and the surface normal. Numerical data of each function is then used to fit the \( ae^{-t/\tau_1} + (1-a)e^{-t/\tau_2} \) function, in which the characteristic time of the longtime behavior is listed in Table S3. A general trend is that water rotation is faster than diffusion, and that the rotation characteristic time is correlated with the desorption characteristic time.

**Table S3.** Relaxation time of water adsorption/desorption (\( \tau_h \)) and water dipole moment rotation (\( \tau_\theta \)). (high cov= high coverage, low cov = low coverage)

| Time | graphene | +H | +O | +OH | +COOH |
|------|----------|----|----|-----|-------|
|      |          | high cov | low cov | high cov | low cov | high cov | low cov | high cov | low cov |
| \( \tau_h \)(ps) | 145 | 258 | 82 | 184 | 120 | 193 | 270 | 796 | 58 |
| \( \tau_\theta \)(ps) | 13 | 18 | 14 | 17 | 15 | 16 | 18 | 19 | 14 |

**S6. Polarizability and forces of the first layer water**
A useful tool to understand the HB strength between water molecules is the distribution of the maximally localized Wannier function (MLWF) center with respect to the distance to the oxygen atom in each molecule. Data from 101 frames over 45 ps trajectories are plotted in Fig. S5.

In Fig. S5(a) we show the distribution function of the MLWF centers of water in the case of pristine graphene. Similar to literature we found two distinct distribution peaks at about
0.32 and 0.50 Å, the MLWFs associated with two lone electron pairs correspond to the former and the ones associated with two bonding electron pairs corresponds to the latter. Consistent with a previous study, there is a shoulder at 0.3 Å in the distribution, as a result of the density functional choice of PBE. We estimate the center and the width of each peak as

\[ r_c = \frac{\int_{r_1}^{r_2} P_r r dr}{\int_{r_1}^{r_2} P_r dr} \]

and

\[ W_{\text{MLWF}} = 2 \left[ \frac{\int_{r_1}^{r_2} P_r (r - r_c)^2 dr}{\int_{r_1}^{r_2} P_r dr} \right]^{1/2} \]

where \( r_1 \) and \( r_2 \) are two bounds of each peak.

The center of the lone electron pair and bonding electron pair peak is found to be at 0.32 and 0.50 (Å), respectively. The corresponding width of these peaks is 3.5 and 2.6 (10^{-2} Å).

With O or H functionalization, there is no clear difference in both \( r_c \) and \( W_{\text{MLWF}} \) compared to the pristine graphene case. However, with OH or COOH functionalization, there are noticeable changes, especially at 0.12 monolayer coverage. Particularly, \( r_c \) of the lone electron pairs is 0.33(Å) and \( W_{\text{MLWF}} \) is 3.9 (on OH-graphene) and 4.3 (on COOH-graphene) (10^{-2} Å). The broadening to the higher distance of the lone electron pair peak is noticeable in Fig. S5(e). This implies that the electrostatic attraction between oxygen of water molecules and proton of neighboring molecules or of functional groups are stronger.

To understand the influence of the surface to the distribution of MLWF centers, we removed the surface atoms from the systems, and calculating again the distribution function. In general, without the surface, the MSWF centers of the lone electron pairs become closer to while that of the bonding electron pairs become more distant from the oxygen nuclei. Most obvious is the case OH or COOH functionalization. Without the surface, \( r_c \) of the lone electron pairs is 0.33(Å) and \( W_{\text{MLWF}} \) is 3.3 (OH) and 3.4 (COOH) (10^{-2} Å). While for the bonding pairs, \( r_c \) is 0.51 (compared to 0.50 with the surface) and \( W_{\text{MLWF}} \) is 3.0 (OH, compared to 2.8 with the surface) and 2.9 (COOH, compared 2.5 with the surface) (10^{-2} Å). The fact is that bonding electron pairs getting closer to proton means the
water molecules become less polarized without the surface. In other words, the OH or COOH functionalized graphene surface polarizes the water layer more strongly, and eventually, acting more forcefully on the water molecules, as shown in the following.

**Figure S5.** Distribution functions of MLWF center relative to the position of oxygen atoms in first layer water molecules on pristine and functionalized (at 0.12 monolayer coverage) in the systems contain both water and surface (s-w) and when the surface is omitted (w).

A quantity helps understand the interaction between water molecules is the force acting on them. Understanding how the surface changes the forces acting on first layer water molecule further provides insight into the diffusion coefficients presented above. As the change in force can correlate with the change in the charge, we determine the force and the density derived atomic point charges, DDAPC.

For each system, we estimated the force change at each molecule as  
$$\Delta F = F(\text{with surface}) - F(\text{without surface}) = \Delta F_O + \Delta F_H + \Delta F_{\text{H}}$$
and similarly, the charge change  
$$\Delta q = q(\text{with surface}) - q(\text{without surface}) = \Delta q_O + \Delta q_H + \Delta q_{\text{H}}.$$
In Fig. S6(a-e) we show the change in the parallel component (xy) of the force against the change in the charge. As it should be clear, $\Delta F_{xy}$ are $\Delta q$ in the case of pristine are small compared to that in functionalized graphene systems. The magnitude of $\Delta F_{xy}$ in the increasing order is $Gr<H<OH$, COOH, which apparently anti-correlates with decrease of the 2D diffusion coefficient $Gr>H>OH$, COOH. It is known that the potential energy surface of a water molecule on pristine graphene surface is relative flat (say, the difference between adsorption sites can be as small as a few meV $^8$), which implies that the 2D force acting on water molecule could be small, consistent with our finding in this study. It is also known that there is a small charge transfer between water and graphene (say $\pm 10^{-3} e$ $^8$), this in part explains the small variation of $\Delta q$ about 0 we found here. With H functionalization, both $\Delta F_{xy}$ and $\Delta q$ become somewhat larger. In our previous study, we showed that an adsorbed H on graphene can increase the adsorption energy of a water molecule on graphene by 80 meV $^9$, meaning that an adsorbed H can act as an attraction center for water on graphene, consequently, increasing the 2D force. There is a weak HB between water and an adsorbed H atom, $^{10}$ by Bader change analysis we estimate that is a reason why $\Delta q$ is broader. With O-, OH-, or COOH- graphene, the potential energy surface of water on graphene becomes rougher, as a consequent of strong HBs between water and the functional groups. This is consistent with the change of MLWF centers shown above. This also makes the magnitudes of $\Delta F_{xy}$ and $\Delta q$ much larger than that in the case of pristine graphene.

Regarding the vertical (z) component of the force, the magnitude is apparently higher than the corresponding parallel (xy) component. In the case of pristine, for example, the z component is about 3-4 times higher. This is because of the fact that the attraction between graphene and water is mainly van der Waals interactions. With functional groups, the attraction is attributed to hydrogen bonding, and also, Van der Waals interaction. As listed in Table S1, the increasing order of vertical diffusion coefficient is COOH $\leq$ OH $< Gr$ $< O$ $\leq$ H, somewhat showing an anti-correlation with the magnitude of $\Delta F$, which follows the decreasing order COOH $\geq$ OH $> Gr$ $\geq$ O $\geq$ H.
**Figure S6.** The difference in the force (the parallel (xy) and perpendicular (z) to surface components) against the difference in the total charge of first layer water molecules on pristine and functionalized (at 0.12 monolayer coverage) in the systems contain both water and surface (s-w) and when the surface is omitted (w). Data obtained from 101 frames over 45 ps trajectories.

**S7. Pb(II) on GO and Pb(II) in water box**
Fig. S7 shows the density of Pb(II) as a function of the distance to the surface in different cases. For Pb(II) on graphene (without water), we took one frame in the trajectory of the graphene case, removed all water molecules, kept Cl(-) ions fixed, then statically relaxed Pb(II) and all C atoms. For Pb(II) in water, we put Pb(II) into a water box with no graphene (with experimental water density), kept Cl(-) fixed, then relaxed the Pb(II)-water system. The equilibrium adsorption distance between Pb(II) and graphene is about 3.0 Å in the absence of water, while in the presence of water, the first maximum position in the distribution of Pb(II) is at 4.2 Å.
**Figure S7.** Density of Pb(II) on surfaces in the liquid phase.

**S8. Coordination number of Pb(II)**

In Fig. S8 we show the relationship between the water/functional group smooth coordination number (CN\_w and CN\_g) of Pb(II) and the distance between Pb(II) and the closest water molecule/functional group (d\_w and d\_g). In the same system, the sum of CN\_w and CN\_g is approximately a constant, thus as Pb(II) approaches the graphene sheet, CN\_w decreases, since spaces around Pb(II) are occupied by functional groups. For H cases, since Pb(II) interacts with H only weakly, CN\_w\-d\_w relationships do not depend on H coverage and show broad distribution. For other cases, the high coverage systems show generally larger CN\_g, smaller CN\_w, and narrower distribution of d\_w. For O, OH, and low coverage COOH cases, CN\_g is always less than 2. For high coverage COOH, CN\_g can reach 4. Plus, the COOH cases have the narrowest distribution of d\_g (less than 3.5 Å), suggesting that the graphene functional groups binds Pb(II) tightly during the simulations. Since carboxyl
groups are much larger than epoxy oxygen atoms and hydroxyl groups, they can be efficient in coordinating with Pb(II).

![Graph showing coordination number of Pb(II) from water and functional groups](image)

**Figure S8. Coordination number of Pb(II) from water and functional groups.**

**S9. Bonding charge density**

To further understand the bonding picture between Pb(II) and the surfaces, and the influence of water in the adsorption, we look at the bonding charge density of Pb(II) with the rest. The bonding charge density was computed as $\Delta \rho = \rho(Pb - R) - \rho(Pb) - \rho(R)$, where $\rho(Pb - R)$, $\rho(Pb)$ and $\rho(R)$ is the electron density of the whole system, of Pb and of the rest (R) of the system, respectively. In Fig. S9 we show the bonding charge density in the case of pristine graphene. Here, we take a frame from its trajectory in such a way that Pb(II) is in a position corresponding to the first peak position in the distribution of Pd(II) shown in Fig. S7. Fig. S9 shows that the charge rearrangement mainly occurs between Pb and surrounding water molecules. There is no contribution from the $\pi$ electron system of
graphene to the bonding charge of Pb(II), showing a significant role of water in the weakened adsorption of Pb(II) on the graphene surface. The electron loss of Pb and electron gain of water (mostly at O atoms) suggests the Pb-water bonds are purely electrostatic, based on strong polarization. As one can expect, the charge rearrangement at water molecules is associated with their lowest occupied and highest unoccupied orbitals.

*Figure S9.* Bonding charge density (isosurface value of 0.01 au, electron gain in blue, electron loss in green) of Pb and the rest of the system on pristine graphene.

**S10. Pb(II) diffusion coefficients**
Diffusion coefficients, Table S4, were computed from the mean square displacement similar to the one described in section S5 for water.

*Table S4.* Diffusion coefficients $D(10^{-5} \text{ cm}^2/\text{s})$ of Pb(II). Gr refers to the non-functionalized graphene for comparison. Gr and H-Gr correspond to rGO, while O-Gr, HO-Gr and HOOC-Gr correspond to GO. The reported values are an average of high and low coverage, since no coverage dependence was observed.

|       | D    | Gr   | H-Gr | O-GO  | HO-GO | HOOC-GO |
|-------|------|------|------|-------|-------|---------|
| Theory| 2.9  | 1.8±0.2 | 0.25±0.4 | 0.14±0.3 | 0.06±0.01 |
| Exp.  | 1.3  |       |       | 1.0   |       |         |

**S11. H$_3$O$^+$ species**
In Fig. S10 we show the radial distribution functional of the H-O pair in the case of COOH-graphene (high coverage) where H is in the functional group and O is in water molecules. The first peak at 1 Å indicates the formation of H$_3$O$^+$. 


**Figure S10.** Radial distribution functional of H-Ow pairs where H is in the COOH functional groups and O is in water molecules.

**S12. Vibrational spectra**

Far infrared spectroscopy analysis shows that upon Pb(II) sorption, there is a change in the spectrum in the range of 0-300 cm$^{-1}$. The characteristic vibration of Pb(II) is observed within this range. In particular, there is an additional peak at 137 cm$^{-1}$ in the spectrum after Pb(II) adsorption. This peak is believed to be associated with the interaction between Pb(II) and graphene oxide. To further elucidate this observation, here we compute the vibrational spectra of O-graphene, OH-graphene, COOH-graphene underlying a water film, with and without Pb(II). The vibration spectrum for each system is computed by the cosine transform of the velocity autocorrelation function, $\text{VDOS} = \int_0^\infty dt \frac{\langle v(0)|v(t)\rangle}{\langle v(0)|v(0)\rangle} \cos(\omega t)$, in which $\langle \cdots \rangle$ indicates the ensemble average over the atoms in functional groups and Pb, and time. In Fig. S11 we show computed spectra. It is clear that in the case of O- and COOH-graphene, the spectrum of each system changes significantly when Pb(II) is included in MD simulations. With O-graphene, the main new peak is at 150 cm$^{-1}$, while with COOH-graphene, the main peak is at 128 cm$^{-1}$. With OH-graphene, we do not see any significant change of the spectrum. This is consistent with the g(r) shown in Fig. 3 (f)-(i), which indicates that Pb(II) interacts more weakly with OH groups and more strongly with COOH or O groups.
Figure S11. Vibrational projected density of states (VDOS) of functional groups from simulations with and without Pb(II). The vertical dashed line indicate the experimental signal position when Pb(II) is introduced, see Ref. 11.

S13. Experimental characterization of adsorbed Pb on GO and reduced GO.

Figure S12. High resolution XPS spectra of C 1s on neat GO and PbCl₂/GO membranes.
Figure S13. The XPS mapping of C 1s (C-C), C 1s (C-O), and Pb 4f measured on the GO membranes filtered with PbCl₂ solution at pH=3-7 (PbCl₂/GO_3 to PbCl₂/GO_7). Each mapping box represents the measurement region of 800 µm x 800 µm on the sample.
**Figure S14.** High resolution XPS spectra of Pb 4f on the PbCl$_2$/GO$_5$ membrane before and after acid wash.
Figure S15. (a) C 1s and Pb 4f XPS spectra taken across GO membranes by partially peeling of GO layers after Pb adsorption and measuring XPS at four different points (P0, P1, P2, and P3); (b) Corresponding changes in atomic concentration of -COOH and adsorbed \(-(\text{COOH})_2\text{Pb}\) as a function of depth across GO determined from C 1s and Pb 4f.
Figure S16. C 1s XPS spectra of (A) as-received graphene oxide and (B) reduced graphene oxide immobilized on glassy carbon.

The major peak at 284.8 eV in Fig. S16(a) is attributed to C=C/C-C bonds. The similar binding energies of the epoxy (C-O-C) and hydroxyl (C-OH) groups make it difficult to deconvolute their respective contributions. These features have been assigned to one combined peak at 286.3 - 286.8 eV.12 The minor peaks at 287.8 and 289 eV are assigned to carbonyl (C=O) and carboxyl (COOH) groups, respectively. Reduction of GO resulted in a ~ 50 % decrease in epoxides and hydroxyls and a ~ 12 % decrease in carboxyls and carbonyls. The new peak at 291.2 eV for rGO, Fig. S16 (b), is the π → π* shakeup satellite peak, which indicates that the aromaticity of graphene is restored during reduction.12
Figure S17. Cyclic voltammograms measured on glassy carbon electrodes immobilized with as-received graphene oxide (GO) and reduced graphene oxide (rGO) in the presence of Pb(II) ions (10 mM PbCl₂ in water used as electrolyte).

Figure S18. XRD results obtained from neat GO and GO membranes after adsorbing Pb(II) at different pH values. The inset table provides the d-spacing values of the GO membranes at each pH.
**Figure S19.** The fitted linear equations describing the permeation of Pb(II) ions per area of GO membrane versus permeate time at different concentrations of the PbCl$_2$ feed solution. Inset figure shows the linear relationship between the feed concentration and permeation rate of Pb(II).

**Table S5.** The calculated Pb(II) permeable rate and diffusion coefficient at different pH and concentrations of PbCl$_2$ in the feed.

| Feed                  | Pb(II) Permeable Rate (mol m$^{-2}$ h$^{-1}$) | Pb(II) Diffusion Coefficient, D$_{CP}$ (cm$^2$ s$^{-1}$) |
|-----------------------|---------------------------------------------|--------------------------------------------------------|
| 2.5 mM PbCl$_2$ at pH=3 | 0.0189                                      | 6.84×10$^{-8}$                                         |
| 2.5 mM PbCl$_2$ at pH=4 | 0.0155                                      | 1.67×10$^{-8}$                                         |
| 2.5 mM PbCl$_2$ at pH=5 | 0.0089                                      | 7.57×10$^{-9}$                                         |
| 12.5 mM PbCl$_2$ at pH=5 | 0.0916                                      | 2.00×10$^{-8}$                                         |
| 25 mM PbCl$_2$ at pH=5  | 0.2094                                      | 2.19×10$^{-8}$                                         |
References

1. Tocci G, Joly L, Michaelides A. Friction of Water on Graphene and Hexagonal Boron Nitride from Ab Initio Methods: Very Different Slippage Despite Very Similar Interface Structures. *Nano Lett* 2014, **14**(12): 6872-6877.

2. Kayal A, Chandra A. Orientational order and dynamics of interfacial water near a hexagonal boron-nitride sheet: An ab initio molecular dynamics study. *J Chem Phys* 2017, **147**(16).

3. Bourg IC, Sposito G. Molecular dynamics simulations of the electrical double layer on smectite surfaces contacting concentrated mixed electrolyte (NaCl-CaCl2) solutions. *J Colloid Interf Sci* 2011, **360**(2): 701-715.

4. Gordillo MC, Marti J. Effect of Surface Roughness on the Static and Dynamic Properties of Water Adsorbed on Graphene. *J Phys Chem B* 2010, **114**(13): 4583-4589.

5. Chen M, Ko HY, Remsing RC, Andrade MFC, Santra B, Sun ZR, et al. Ab initio theory and modeling of water. *P Natl Acad Sci USA* 2017, **114**(41): 10846-10851.

6. Ulman K, Busch S, Hassanali AA. Quantum mechanical effects in zwitterionic amino acids: The case of proline, hydroxyproline, and alanine in water. *J Chem Phys* 2018, **148**(22).

7. Blochl PE. Electrostatic Decoupling of Periodic Images of Plane-Wave-Expanded Densities and Derived Atomic Point Charges. *J Chem Phys* 1995, **103**(17): 7422-7428.

8. Freitas RRQ, Rivelino R, Mota FD, de Castilho CMC. DFT Studies of the Interactions of a Graphene Layer with Small Water Aggregates. *J Phys Chem A* 2011, **115**(44): 12348-12356.

9. Nguyen MT, Phong PN. Accelerating Dynamics of H on Graphene by Coadsorbates. *J Phys Chem A* 2017, **121**(29): 5520-5523.

10. Erni R, Rossell MD, Nguyen MT, Blankenburg S, Passerone D. Stability and dynamics of small molecules trapped on graphene. *Phys Rev B* 2010, **82**(16).

11. Wang XX, Chen ZS, Yang SB. Application of graphene oxides for the removal of Pb(II) ions from aqueous solutions: Experimental and DFT calculation. *J Mol Liq* 2015, **211**: 957-964.
12. Bagri A, Mattevi C, Acik M, Chabal YJ, Chhowalla M, Shenoy VB. Structural evolution during the reduction of chemically derived graphene oxide. *Nature chemistry* 2010, 2(7): 581-587.