Controlling extra charge carriers is pivotal in manipulating electronic, optical, and magnetic properties of various two-dimensional materials. Nonetheless, the ubiquitous hole doping of two-dimensional materials in the air and acids has been controversial in its mechanistic details. Here we show their common origin is an electrochemical reaction driven by redox couples of oxygen and water molecules. Using real-time photoluminescence imaging of WS\textsubscript{2} and Raman spectroscopy of graphene, we capture molecular diffusion through the two-dimensional nanoscopic space between two-dimensional materials and hydrophilic substrates, and show that the latter accommodate water molecules also serving as a hydrating solvent. We also demonstrate that HCl-induced doping is governed by dissolved O\textsubscript{2} and pH in accordance with the Nernst equation. The nanoscopic electrochemistry anatomized in this work sets an ambient limit to material properties, which is universal to not only 2D but also other forms of materials.
Reduction in dimensions has seen many scientific discoveries in various metallic and semiconducting low-dimensional materials during the past four decades. Because of their high fraction of surface atoms, in particular, various material properties of two-dimensional (2D) materials are greatly affected by charge exchange with neighboring chemical entities or environments. When exposed to alkali metals or halogens, for example, the Fermi level ($E_F$) of graphene swaps by several tenths of 1 eV with a substantial change in electrical conductivity or optical absorption. Such chemical modification of the electronic structure allows detection of even a single molecule that adsorbs on graphene in a transistor form. The charge exchanges can be described by a simple donor–acceptor model by assuming a significant difference in their electron affinities. Despite the apparent simplicity, however, there is a clear lack of understanding in the ubiquitous chemical interactions of 2D materials. The first graphene transistor was reported to be doped with hole carriers originating from unknown chemical entities. Optical confirmation soon followed this observation, but with no complete mechanistic understanding. While various acids were explored to inject hole carriers in graphene, their exchange mechanism is not clear. All of these underline that the spontaneous charge transfer between 2D materials and the environment is far from being understood, which hampers both fundamental research and application of 2D materials. In this work, we elucidate that the charge exchange is driven by redox couples of oxygen and water molecules, originally proposed for surface conduction of diamond and that the redox reaction is confined within the nanoscopic space between 2D materials and hydrophilic substrates. By exploiting environment-controlled in situ spectroscopy, we captured molecular diffusion through the interstitial 2D space and revealed that photoluminescence (PL) of WS$_2$ and lattice vibration of graphene, both as an indicator of charge density, are dictated by oxygen and water contents and their spatiotemporal distribution.

Results
Chemically modulated ionization of excitons. Single-layer WS$_2$ (1LW$_{\text{silica}}$) was mechanically exfoliated onto SiO$_2$/Si substrates (see the “Methods” section) and served as a model 2D system with precise control over gas environments (Fig. 1a and Supplementary Fig. 1). Photogenerated excitons (X$^0$) have substantial binding energy due to dimensionally restricted screening and can interact with excess charge carriers to form charged excitons or trions (X$^\pm$) with additional stabilization as depicted in Fig. 1b. As shown in Fig. 1c, the PL spectra of 1LW$_{\text{silica}}$ in the ambient air typically showed two peaks, each originating from excitons (X$^0$ at $E_X$ = 2.01 eV) and negative trions (X$^-$ at $E_X$ = 1.98 eV), the latter of which derived from defect-related native charge carriers. By assuming that the ionization reactions of excitons into trions are governed by the law of mass action, their PL intensity ratio ($I_{X^-}/I_{X^0}$) serves as a quantitative measure for the density of charge carriers that are modulated by chemical interaction between WS$_2$ and the environments (Supplementary Note 1). When the optical gas cell was purged with an Ar gas, $I_{X^-}/I_{X^0}$ increased noticeably, which indicated an increase in electron density ($n_e$). The concomitant decrease in the total intensity ($I_t = I_{X^0} + I_{X^-}$) is due to the increasing importance of the nonradiative decay channel at higher $n_e$. Water vapor in the Ar gas, however, reduced $n_e$ when judged from a noticeable decrease in $I_{X^0}/I_{X^-}$. Exposure to dry or humid O$_2$ led to an even more considerable decrease in the ratio, and thus further depletion of negative carriers. Time-lapse measurements in Fig. 1d showed that the total PL intensity varied reversibly between Ar and O$_2$ atmospheres, which confirmed the molecular origin of the charge modulation.

The dissociation energy of the trions ($E_{\text{diss}} = E_{X^0} - E_{X^-}$) showed a strong correlation with the intensity ratio over the entire atmospheric conditions (Fig. 1e). The overall trend is similar to what was observed in electrically gated measurements as shown in Fig. 1e. Since $E_{\text{diss}}$ is linearly dependent on the Fermi level, smaller $E_{\text{diss}}$ for the oxygenic or humid atmosphere indicates significant depletion of electrons induced by hole doping of WS$_2$ by O$_2$ or H$_2$O. Judging from $E_{\text{diss}}$ given as a function of $I_{X^-}/I_{X^0}$ in Fig. 1e, the depletion was near completion, and an injection of additional hole carriers would lead to emergence of positively charged trions. A typical difference in $n_e$ was $3 \times 10^{13}$ cm$^{-2}$ between Ar and wet Ar$_2$O$_2$ environments (see Supplementary Note 1 for estimation of charge density).

Spatially resolved spectroscopy showed that the O$_2$-driven rise in $I_{X^-}$ was faster at edges than inner areas that are a few micrometers off the edges (Supplementary Fig. 2). Moreover, 1LW$_{\text{BN}}$ (dry-transferred onto a thin hexagonal BN crystal, hBN) exhibited a much smaller $I_{X^-}$ and O$_2$ sensitivity than 1LW$_{\text{silica}}$ (Fig. 1d). All of these spectral changes indicate that the density of charge carriers is reversibly modulated by a certain charge transfer (CT) reaction that involves O$_2$ and water. The site and substrate-dependent kinetics suggested that the reactions are localized at the interface between WS$_2$ and substrates.

Interface-confined nanoscopic redox reactions. Wide-field PL imaging revealed how the CT reaction evolved in space and time as shown in Fig. 2, where 1LW samples were uniformly illuminated with 514-nm laser light under controlled gas or liquid environments. In the ambient air, the intensity image of 1LW$_{\text{silica}}$ exhibited slight local irregularities over the entire sample area of ~70 μm$^2$ (Fig. 2a). The multilayer neighbors showed negligible emission due to their indirect bandgaps. Because of the O$_2$-driven CT reaction mentioned above, the overall intensity decreased ~50% in an Ar gas and was recovered within 20 min under O$_2$ flow, which is consistent with the reversibility shown in Fig. 1d. Notably, however, the recovery in Fig. 2a showed an evident edge-to-center propagation as shown in the enhancement images that are normalized by that of the deoxygenated state in Ar. Exposure for 10 s led to a sharp enhancement by ~30% at the two edges with the other two connected to the multilayers remaining silent. Within 60 s of O$_2$ flow, the two edges exhibited ~100% enhancement, and the enhancement fronts moved further gradually reaching a steady state after 20 min (Supplementary Movie 1; Supplementary Fig. 3 for more examples) followed by its reversal in subsequent Ar flow (Supplementary Movie 2). In contrast, neither directional enhancement nor complete recovery was observed for 1LW$_{\text{BN}}$ (Fig. 2c). On average, the enhancement was small (20–30%) and occurred rather uniformly, which agrees with Fig. 1d. All of these observations indicated that the CT reactions diffuse through the WS$_2$–silica interface as illustrated by the thick black arrow in Fig. 2d. Noting that the upper surfaces of samples were accessible to the reactants, these results implied a crucial role of the interface or surface of silica, and led us to a mechanistic model with two essential ingredients. First, we explain that charge density of WS$_2$ is modulated by the redox reaction involving oxygen and water

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O,$$

where reduction of O$_2$ is accompanied by oxidation (hole doping) of WS$_2$ (see Supplementary Note 2 for a detailed account on CT at the solid–liquid interface based on Gerischer model). The reaction in Eq. (1) was validated for surface transfer doping of hydrogenated diamonds, the electrochemical nature of which was first proposed by Maier et al. Similar observations were also made for other material systems including GaN, ZnO, carbon
nanotubes\textsuperscript{20}, and graphene\textsuperscript{21}. Second, the CT reaction is localized at the nanoscopic interface by hydrophilic surface functional groups of SiO\textsubscript{2} that accommodate water molecules because of the energy gain by hydration of ionic species.

Under this model, the directional propagation of the PL enhancement (Fig. 2a and Supplementary Movies 1 and 2) indicates that the rate-determining step is not the CT reaction but the diffusion of the CT reactants. It is to be noted that the CT rate will decrease with the reaction proceeding according to a simple theory for the CT reaction (Supplementary Note 2). As depicted by the black arrow in Fig. 2d, the diffusion of O\textsubscript{2} through WS\textsubscript{2}-silica interface is initiated from the edges and substantially hindered because of the narrow interfacial gap. The typical propagation rate for 1LW\textsubscript{silica} was \(\sim 1\ \mu\text{m}\ \text{min}^{-1}\) with a notable variation among samples (Supplementary Fig. 3). On the other hand, the substantially reduced O\textsubscript{2} sensitivity of 1LW\textsubscript{BN} (Figs. 1d and 2c) can be attributed to the less hydrophilic nature of hBN that does not hold sufficient water molecules required for the redox reaction (Fig. 2f). In addition, the effective interstitial gap in 1LW\textsubscript{BN} will be much smaller than that in 1LW\textsubscript{silica} because of the flatter substrates and consequently enhanced adhesion for the former, and thus interfacial diffusion of oxygen required for CT will be greatly attenuated. This model is also supported by the substantially enhanced O\textsubscript{2} sensitivity and nondirectional PL enhancement of 1LW\textsubscript{silica} immersed in water. As shown in Fig. 2b, its PL intensity was increased by \(\sim 200\%\) in the presence of dissolved O\textsubscript{2}, but the enhancement did not show any noticeable spatial propagation (Supplementary Movies 3 and 4). Unlike the gas-phase reaction (Fig. 2d), the top surface of WS\textsubscript{2} is in direct contact with water that serves as a hydrating solvent and thus works as a major CT route as illustrated by the thick blue arrow in Fig. 2e.

Boosting and quenching of redox reactions. To unveil the pivotal role of hydrophilic SiO\textsubscript{2} surface in the redox reaction, we exploited charge-density-dependent phonon hardening of graphene. As shown in Fig. 3a, G and 2D peaks (\(\omega\text{G}, \omega\text{2D}\)) of 1L graphene/SiO\textsubscript{2}/Si (1LG\textsubscript{silica}) were greatly upshifted and recovered by thermal annealing at 500 and 1000 °C, respectively. Based on the established Raman metrology\textsuperscript{22} of hole density (\(n\text{h}\)) and lattice strain (\(\varepsilon\)) shown in Fig. 3b, \(\omega\text{G}\) and \(\omega\text{2D}\) of samples that were treated at various temperatures were translated into \(n\text{h}\) and \(\varepsilon\) with high accuracy of \(\sim 1 \times 10^{12}\ \text{cm}^{-2}\) and \(\sim 0.2\%\), respectively (Fig. 3c).

Despite many studies\textsuperscript{23–27} however, the mechanistic origin of the thermally activated CT or hole doping has been unclear. In the following section, we propose and show that it is the same redox reaction as Eq. (1), and thermal activation renders SiO\textsubscript{2} surface hydrophilic enough to bind a certain amount of water molecules. As illustrated in Fig. 3e (left), the surface of silica is terminated with hydrophilic siloxane (Si–O–Si) and hydrophilic silanols (Si–OH). At elevated temperature, the latter transforms into the former without the presence of water (dehydration) and vice versa with water (hydroxylation)\textsuperscript{28}. When annealed at \(\sim 750\ °\text{C}\), the SiO\textsubscript{2} surface becomes hydroxylated at the expense of water trapped during sample preparation. When placed in the ambient air, more water molecules are attracted at the graphene–SiO\textsubscript{2} interface as depicted in Fig. 3e (middle), and electrons of graphene are consumed by the interfacial redox reaction leaving

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**Fig. 1** Chemically modulated ionization of excitons. a In situ optical measurements of single-layer (1L) WS\textsubscript{2} supported on SiO\textsubscript{2} (1LW\textsubscript{silica}) located in a controlled gaseous environment. The scheme illustrates 1LW\textsubscript{silica} interacting with O\textsubscript{2} and water in a redox reaction. b Electronic energy bands of WS\textsubscript{2} with neutral (X\textsuperscript{0}) and charged (X\textsuperscript{–} and X\textsuperscript{+}) excitonic states (bottom panel); schematic representation of their radiative and nonradiative (nr) decay rates (\(\gamma\)) given as a function of charge density (\(n\text{e} \text{and} n\text{h}\)) (ref. 14) (upper panel). c Photoluminescence (PL) spectra of WS\textsubscript{2} in various gas environments. Solid lines are double Lorentzian fits representing X\textsuperscript{0} and X\textsuperscript{–}. Relative humidity for wet gases was 45%. d Time-lapse measurements of PL intensity of 1LW\textsubscript{silica} and 1LW\textsubscript{BN} in response to changes in gas environments: ambient air (white box), Ar (yellow box), and Ar:O\textsubscript{2} = 4:1 (blue box). e Equivalence between chemical (filled symbols) and electrical (lines, refs. 15,16) modulations of charge density in WS\textsubscript{2}, where trion dissociation energy (\(E\text{diss}\)) in the left ordinate was given as a function of PL intensity ratio (X\textsuperscript{–}/X\textsuperscript{0}). The electron density (\(n\text{e}\)) in the right ordinate (open symbols) was determined for the filled symbols according to the mass action law for excitons and trions (Supplementary Note 1).

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**Fig. 2** Photoluminescence (PL) intensity (a.u.) of X\textsuperscript{–}/X\textsuperscript{0} as a function of PL intensity ratio (X\textsuperscript{–}/X\textsuperscript{0}) and electrical (lines, refs. 15,16) modulations of charge density in WS\textsubscript{2}, where trion dissociation energy (\(E\text{diss}\)) in the left ordinate was given as a function of PL intensity ratio (X\textsuperscript{–}/X\textsuperscript{0}). The electron density (\(n\text{e}\)) in the right ordinate (open symbols) was determined for the filled symbols according to the mass action law for excitons and trions (Supplementary Note 1).
thickness of each arrow represents the relative contribution of each pathway to the overall charge transfer reactions.

CT reaction can be generalized to a pH-dependent redox between pH-controlled redox reactions. The activated CT.

water is required for the thermal hydroxylation, which leads to obtained by dividing PL images with those for time zero. Samples in areas (dashed lines) were given in the Supplementary Fig. 4 for raw data). As shown in Fig.3c, measuring water-contact angles (WCA) for bare substrates (see section between hydroxylation and dehydroxylation was veri... expressed on the activated CT.

graphene highly hole-doped. When treated at >750 °C, however, dehydroxylation was more dominant as shown in Fig. 3e (right), and Δn_h dropped to 1/3 of the maximum (Fig. 3b, c). Competition between hydroxylation and dehydroxylation was verified by measuring water-contact angles (WCA) for bare substrates (see Supplementary Fig. 4 for raw data). As shown in Fig. 3c, Δn_h has a clear correlation with WCA and thus hydrophilicity of substrate... surfaces. To further corroborate the hypothesis, we prepared samples in a glove box with interfacial water further minimized by pretreating substrates with diethyl zinc vapor that removes even trace amounts of surface water29. The charge-density maps obtained after annealing at 400 °C showed that CT is negligible for diethyl zinc-treated samples unlike non-treated samples (Fig. 3d). This control experiment confirmed that interfacial water is required for the thermal hydroxylation, which leads to the activated CT.

pH-controlled redox reactions. We now show that the interfacial CT reaction can be generalized to a pH-dependent redox between 2D materials and O2 dissolved in liquid water. High-purity O2 or Ar gas was sparged through an optical liquid cell containing HCl solution of a preset pH to control the concentration of dissolved O2 (Fig. 4d). When O2 was introduced to the Ar-saturated HCl solution of a preset pH to control the concentration of dissolved O2 (Fig. 4a). Notably, n_h decreased reversibly with Ar gas bubbled through the solution, and the doping–undoping cycle could be repeated multiple times. The O2-mediated CT was observed at pH = 1–4 but not at pH ≥ 5 (Supplementary Fig. 5). The rise and decay kinetics of n_h are highly pH-dependent and self-limited (Fig. 4b, c). A typical initial CT rate is ~1 × 10^10 cm^-2s^-1 at pH = 2 and [O2] = 1.3 mM (see Methods). As shown in Fig. 2b, PL signals of WS2 also exhibited the same sensitivity toward dissolved O2 in water, and the change became more obvious at lower pH (Fig. 4f and Supplementary Fig. 6). Eq. (1) shows that one oxygen molecule may exchange four electrons with other materials in the presence of protons. According to the Gerischer model on CT at an electrode–liquid
interface\(^3\), the direction of CT is determined by energetic alignment between the Fermi level \((E_F)\) of 2D materials and electrochemical potential \((E_{F,\text{redox}})\) of the redox system as shown in Fig. 4e (Supplementary Note 2). Since \(E_{F,\text{graphene}} = -4.57\) eV and \(E_{F,\text{redox}} = -5.669 + 0.0592pH - 0.0148 \log[p(O_2)]\), reduction of \(O_2\) is more favored at lower pH, which leads to increased hole doping of graphene (Supplementary Note 2). On the other hand, the CT is doubly inhibited by a reduction of the reactant and an increase in \(E_{F,\text{redox}}\), when the concentration of \(O_2\) is decreased. The rate of CT is proportional to the density overlap between occupied states of graphene and empty oxidized states of the redox system, the latter of which is depicted as a Gaussian distribution centered at \(E_{\text{ox}}\) in Fig. 4e. The self-limited CT observed even in the presence of sufficient reactants (Fig. 4b) is due to the CT-induced decrease in \(E_{F,\text{graphene}}\), and can be well described by the Gerischer model (Supplementary Note 2). For WS\(_2\) that is natively \(p\)-doped by various defects including S vacancies\(^3\), its Fermi level is near the conduction band minimum located at \(-3.93\) eV\(^2\) that is 0.64 eV higher than that of graphene. Thus, CT from WS\(_2\) to the redox couples of \(O_2/H_2O\) is more favorable than from graphene, which is consistent with our finding that the pH threshold for \(O_2\)-induced CT is higher for WS\(_2\) than that for graphene.

**Discussion**

In this work, we have shown that the ambient oxygen reduction reaction is behind the long-standing mystery of the spontaneous and activated CT doping in graphene and WS\(_2\). Redox couples of \(O_2/H_2O\) responsible for the CT reside at the interface of 2D materials and substrates, and their 2D diffusion was captured in real time by wide-field PL imaging. The CT reaction can be turned on and off via controlling \(O_2\) or interfacial water serving as a hydration solvent. The CT rate of 2D materials in contact with liquid water can also be tuned by varying the concentration of dissolved protons or \(O_2\) as described by the Nernst equation. The presented nanoscopic electrochemistry will pave the way toward efficient control of charge density and the related material properties in 2D, and other low-dimensional materials and devices.

**Methods**

**Preparation and treatment of samples.** Most of single-layer WS\(_2\) (1LW\(_{\text{silica}}\)) and graphene (1LG\(_{\text{silica}}\)) samples were prepared by mechanically exfoliating bulk crystals (WS\(_2\) from 2D semiconductors Inc.; graphite from Covalent Materials Inc. and Naturgraphit GmbH) onto SiO\(_2\) (285 nm)/Si substrates in the ambient environment. For 1LW\(_{\text{BN}}\) samples, single layers were first mechanically exfoliated onto polydimethylsiloxane substrates and then dry-transferred onto thin hBN crystals supported on SiO\(_2\)/Si substrates. To minimize a change in spectroscopic signals induced by optical interference, hBN crystals thinner than 3 nm were selected as substrates. To remove interfacial water in 1LG\(_{\text{silica}}\), we exposed bare substrates briefly to the vapor of diethyl zinc before mechanical exfoliation in a glove box. For thermal activation, samples were annealed at a target temperature for 2 h in a quartz tube furnace that was maintained at a pressure of 3 mTorr.

**Raman and PL measurements.** Raman and PL were performed with a homebuilt micro-Raman spectrometer setup\(^3\). Briefly, monochromatic outputs from solid-state lasers operated at 458 and 514 nm were focused onto samples with a spot size of \(\sim 1\) \(\mu\)m by using a microscope objective (40×, numerical aperture = 0.60). Backscattered PL and Raman signals were collected with the same objective and guided to a spectrometer equipped with a liquid nitrogen-cooled CCD detector. Overall spectral accuracy was better than 5 and 1 cm\(^{-1}\) for PL and Raman measurements, respectively. To avoid significant photoinduced effects, we maintained the average power of the excitation beam below 6 \(\mu\)W for WS\(_2\) and 400 \(\mu\)W for graphene samples.
H2O redox couples. Electron-accepting oxidized states are represented by Gaussian distributions displaced from ncell with a gas sparger combined to a micro-spectroscopy setup. states originating from defects. solid lines are exponential concentration of dissolved oxygen was controlled by an area with a diameter of ~100 m. PL signals in the range between 1.9 and 2.1 eV mostly contributed to the PL images recorded with the CCD detector.

Control of gas and liquid environments. For optical measurements in controlled gas environments, samples were mounted in a custom-made optical gas cell with precise controls over the flow rates of Ar (20–1000 mL min⁻¹) and O₂ (5–250 mL min⁻¹). Unless otherwise noted, flow rates for dry gases were 1000 and 250 mL min⁻¹ for Ar and O₂, respectively. Relative humidity (RH) inside the gas cell was monitored by a serially connected hygrometer and could be controlled between 5 and 90% by varying the mixing ratio of an additional Ar gas line that passed through a water bubbler (Supplementary Fig. 1a). The temporal change in RH upon injection of wet gas could be well fitted with two exponential functions with time constants of 15 ± 2 and 116 ± 40 s. The fast component is limited by the finite flow rate through the gas manifold, and the slower one is related to adsorption kinetics of water on the inner walls of the manifold and gas cell. The former time constant set an upper bound for the average arrival time for the dry adsorption kinetics of water on the inner walls of the manifold and gas cell.

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