Photooxidation and quantum confinement effects in exfoliated black phosphorus


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A. METHODS
A1- Exfoliation of Black Phosphorous (P(black))
Mono-, bi- and multilayer 2D-phosphane (i.e. monolayer of black phosphorus and also called phosphorene) were exfoliated from 99.998% pure black phosphorus (Smart Elements) using a procedure derived from the scotch-tape exfoliation technique1. The modified exfoliation procedure involved two polydimethylsiloxane (PDMS) stamps, as depicted in Figure S1. The first PDMS stamp was reticulated in a petri dish and the second one was reticulated in a cylindrical tube of 1 cm diameter. As described in the main text, the exfoliation was done in a dark room or in a glove box under nitrogen flux.
Figure S1 | Three step exfoliation procedure of P(black). Step 1: Exfoliation done on the flat PDMS-1. Step 2: The flakes were reported on semi-spherical PDMS-2 stamp. Step 3: the stamp was rolled on the substrate (SiO\textsubscript{2} on Si) with an estimated speed of 0.1 cm/s.

A2- Optical contrast measurements of n-layer 2D-phosphane

The flakes were localized and characterized under an optical microscope (Olympus BX51) placed in a glove box using red light (glass colored optical filter 580 nm) to limit the photo-oxidation of the flakes and enhance the contrast. The optical contrast, $C_{\text{red}}$, was measured preferentially at the center of the image and using the following:

$$C_{\text{red}} = \frac{R_{\text{sub}} - R_{\text{flake}}}{R_{\text{sub}}},$$  \hspace{1cm} (S1)

where $R_{\text{sub}}$ and $R_{\text{flake}}$ are the reflection signals on the substrate and flake respectively. Some examples of multilayer 2D-phosphane thus produced are presented in Figure S2.

Figure S2 | Examples of optical micrographs of the localization of flakes of multilayer 2D-phosphane using different optical contrasts.
A3- Measurements of the layer thickness using atomic force microscopy (AFM)

The substrate used is a 305 nm (or 291 nm) SiO₂ grown on a n++ Si wafer that was previously patterned with metallic alignment marks by photolithography. Short time before exfoliation, the substrate was annealed at 300°C for 3 hours and then quickly placed in a glove box equipped with an optical microscope fitted with a glass colored optical filter 580 nm and an AFM instrument (Auto Probe CP, ThermoMicroscopes). The exfoliation procedure, as well as optical and AFM characterizations of the exfoliated P(black) flakes, were all done in the same glove box under a continuous flow of nitrogen (i.e. no contact with ambient air). The thicknesses of the flakes was measured using intermittent imaging mode at 85% damping with silicon cantilever probes (ACTA from AppNano, Si probes with Al coating, tip radius < 10 nm, spring constant 25-75 N/m). The experimental procedure in the glove box established a correlation between optical contrasts and average thicknesses of different flakes and the results for many different flakes are presented in Figure S3.

Figure S3 | Evolution of the optical contrast as a function of the AFM thickness for many multilayer 2D-phosphanes on two different substrates. Red and blue: Results for SiO₂/Si substrates with oxide thicknesses of 291nm and 305 nm, respectively.
A5 - Raman Setup:

The Raman spectrometer is custom built and is composed of a laser line at 532 nm (Centenia laser), a 50X (NA 0.5) objective and a nitrogen cooled charged-coupled device camera (JY Symphony) mounted on a Jobin-Yvon Triax 550 Spectrometer (grating 1800 g/mm blazed at 450-880 nm). The spectral region probed was between 200-550 cm\(^{-1}\) with a precision of ± 0.2 cm\(^{-1}\). The sample stage was equipped with a cryostat (Janis ST500) coupled to a gas manifold and a pump. The vacuum pressure inside the cryostat chamber was below 2 x 10^{-5} Torr. The gases introduced in the chamber were oxygen (leak of ~0.5 Torr) and water vapor at partial pressures of 475 Torr and 13 Torr, respectively. The deionized water used in this experiment was previously deoxygenated using several freeze thaw cycles during pumping.

A6 – Methods of Photo-oxidation Monitoring:

i) AFM monitoring of oxidation:

A simple way to follow the progression of the photo-oxidation of flakes was to compare a sequence of optical microscopic images at different exposure times while continuously illuminating with a bright lamp in air. Bumps distributed at the surface of the flake formed several minutes after exposure are shown in Figure S4. AFM measurements in similar conditions also reveal the presence of bumps even before they become visible in the optical microscope (See for instance Figure 1a in the main text).

![Figure S4](image)

Figure S4 | Optical microscopy images of a multilayer 2D-phosphane on SiO\(_2\)/Si substrate taken just after exfoliation (left) and few hours in air with constant light exposure (right).
ii) In-situ Raman measurements of oxidation (transparent layers):

We probed the Raman intensity with time (Figure 1 main text) in order to assess the kinetics of degradation and this is justified as follows: By definition, the Raman intensity is linked to the Raman cross-section, \( \sigma \) [in units of cm\(^2\) per atom], using \( I = \sigma I_{\text{inc}} \), where \( I \) [W] is light intensity produced by the scattering process and \( I_{\text{inc}} \) [W cm\(^{-2}\)] is the power density of the incident light at the atomic position. Assuming that \( I_{\text{inc}} \) is constant for a fixed laser position, \( I \) measures the kinetics because \( I \) is proportional to the number of scatterers (here pristine P atoms). The approximation is however valid only for flakes that are mostly transparent, i.e. when they are thin enough so that the light absorption varies by only few percent during the degradation process. This approximation is not valid for bulk samples because degradation will modify the depth of analysis due to increased light penetration into the sample.

As shown in the Figure S5, the samples were placed in a buffer solution maintained at pH of 5.8 using phosphoric acid and sodium hydroxide. To minimize the laser path length through the solution, a cover glass slide was placed close to the sample with a PDMS donut on top. The slide was isolated from the solution using a PDMS donut as shown in Figure S5.

![Figure S5](image-url) | Scheme of the experimental setup for the Raman experiments in deionized water.
A7 – AFM images of monolayer and bilayer 2D-phosphane

AFM images of monolayers and bilayers are shown in Figure S6 – note that the samples in Figures S6c-d are those used for the Raman spectra shown in Figure 4 (main text). The monolayer in Figure S6a-b was first isolated, but its small size did not allow for optical contrast measurements. The Raman spectrum of that monolayer was obtained, but the position of the laser spot (at 532 nm, NA 0.55) had to be located on the upper corner (see location in Figure S6b) in order to avoid signals from the multilayers that are adjacent to it. To ensure a good signal-to-noise ratio, long acquisition time (20 min) at a fluence of 100 µW.µm⁻² was required in that case due to the small overlap of the laser beam with the monolayer. The second monolayer (Fig. S6c) has much larger dimensions, which enabled easy measurements of both optical contrast and Raman spectra at different temperatures.

Figure S6 | AFM images of a bilayer and monolayers. a and b: The Monolayer 1 and a zoom to illustrate the laser position during Raman measurements. c: AFM image of Monolayer 2 used for the Raman spectrum shown in Figure 4 (main text). d: Bilayer 4 for the Raman spectrum in Figure 4 (main text). The thicknesses are Monolayer 1 (1.1±0.1 nm), Monolayer 2 (0.8±0.1 nm) and Bilayer 4 (1.4±0.1 nm).
B. ADDITIONAL EXPERIMENTAL RESULTS

B1 – Raman Results

Figure S7 | Kinetics of photo-oxidation of a multilayer 2D-phosphane at different pH. Evolution of the $A_g^2$ integrated Raman intensity ($\lambda = 532$ nm) of multilayer 2D-phosphane placed in a buffer solution and maintained at pH of 7.8, 6.8 and 5.8, respectively.

Figure S8 | Evolution of the $A_g^2$ integrated Raman intensity ($\lambda = 532$ nm) of multilayer 2D-phosphane under different gas exposures. The laser illumination is at a wavelength of 532 nm and a fluence of 200 $\mu$W.\(\mu\)m$^{-2}$. 
Figure S9 | Dependence of the full-width at half maximum (FWHM) of the $A^2_g$ mode during photo-oxidation ($\lambda=532$ nm). a Comparison of the Raman intensity of a 5nm thick flake just after exfoliation and after a laser exposure of one hour with a fluence of 100 $\mu$W.$\mu$m$^{-2}$ ($\lambda=532$). b-c Optical image of the multilayer 2D-phosphane at t=0 and at the end of the laser exposure. The difference in background coloration between (b) and (c) comes from the objective lens used to take the picture, 50X and 20X, respectively. d Evolution of the FWHM of the $A^2_g$ mode as a function of time exposure.
Figure S10 | Fit to Raman spectra ($\lambda = 532$ nm) of the trilayer and 5-layer 2D-Phosphane to illustrate the presence of a broad feature in the region of $B_{2g}$ and $A_g^2$ modes after photo-oxidation in ambient conditions. a: Trilayer taken after 45 sec and 60 min of photo-oxidation under a bright lamp in ambient conditions. b: 5-layer 2D phosphane after degradation in air.

Figure S11 | Raman experiments at $\lambda = 532$ nm on Trilayers 2D-Phosphane. a, Raman spectra of Trilayer 3 at 300K and 77K. b, Polarization-resolved integrated Raman intensities of $A_g^1$, $B_{2g}$ and $A_g^2$ a trilayer, excited at a polarization corresponding to the $A_g^2$ intensity maximum. c, $A_g^1/A_g^2$ ratio evolution as a function of time exposure to a bright lamp in ambient conditions of Trilayer 2 and 3. We note that the intensity of the $B_{2g}$ mode changes also, but comparison is complicated by different polarization rules.
Figure S12 | Collection of Raman spectra (λ = 532 nm) from different \( n \)-layer 2D-phosphane at room temperature and 77K. The AFM thickness are; Monolayer 1 (1.1±0.1 nm), Monolayer 2 (0.8±0.1 nm), Bilayer 1 (1.5±0.1 nm); Bilayer 2 (1.2±0.1 nm); Bilayer 4 (1.4±0.1 nm); Trilayer 1 (1.9±0.1 nm); Trilayer 2(1.8±0.1 nm); Trilayer 3(1.9±0.1 nm); 4-layer(2.6±0.1 nm); 5-layer(3.2±0.1 nm).
Figure S13 | Evolution of the full-width at half maximum (FWHM) and peak shift of the $A_g^1$, $B_{2g}$ and $A_g^2$ Raman modes of many $n$-layer 2D-phosphane as a function of thickness. a, FWHM and b, Raman shift. Note that AFM thicknesses of more than 4 nm were obtained from optical contrast plot in Fig. S3.

B2– Transmission electron microscopy (TEM) imaging and spectroscopies

i) Microscope characteristics. TEM and high-angle annular dark-field (HAADF) STEM images were recorded with a Libra 200 MC Zeiss operating at 200 kV and at 80 kV. The microscope is equipped with a monochromatic Schottky FEG source delivering an energy resolution down to 150 meV and a Gatan Ultrascan camera. Point resolution is 2.3 Å and information limit is 1.2 Å at 200kV. The TEM can operate in scanning mode (STEM) with a spatial resolution under 1 nm and is equipped with Bright Field (BF) and HAADF detectors. Finally the machine is equipped with an in-column energy filter making possible energy filtered TEM (EFTEM), EELS measurements in Scanning TEM mode and acquisition of spectrum imaging datacubes (or hyperspectral EELS).

ii) Exfoliation of P(black) on the TEM grid. P(black) exfoliation was carried out using PDMS stamps in a low-light “dark” room. After three exfoliation steps, the grid was delicately placed in
contact with the PDMS stamp to transfer thin layers on the carbon thin film of the grid for TEM analysis.

**iii) Simulations of High Resolution TEM (HRTEM) images.** Experimental HRTEM images were simulated using the JEMS software with the following TEM parameters:

**Table S1:** Parameters used in JEMS software to simulate HRTEM images

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**iv) TEM Analysis and EELS measurements of pristine layers.** Different samples of exfoliated P(black) were prepared in ambient conditions under dim light and quickly transferred on a TEM grid for structural analysis. Figure S14 presents TEM images of monolayer and multilayer 2D-phosphane, Fast Fourier Transforms (FFT) of selected areas, and image simulations of the layered structure projected along different orientations. The exfoliation provided micrographs with top and side views. The puckered structure of multilayer 2D-phosphane is clearly revealed in Figure S14d, thanks to a fold in the layers that provides a view along the \( b \)-axis. The structure is confirmed by both the analysis of the FFT pattern of the selected area and the image simulation of the layered structure viewed along the (201) zone axis. The same can be said for the monolayer and multilayer in Figure 14b and viewed along the \( c \)-axis ((110) zone axis). From the image simulations shown in Figure 14a, the stacking of the layers can be distinguished and monolayer 2D-phosphane identified. Furthermore, TEM-EELS core-loss analysis at the phosphorus K and L edges revealed that the sample essentially consists mostly of pure phosphorus (i.e. with oxygen content of less than 1%). Scanning TEM High Angle Annular Dark Field (STEM-HAADF, Figure S14e), which intensity is proportional to the number of phosphorus planes, was used to determine the thickness and the structural integrity of the samples.
iii) Simulations of High Resolution TEM (HRTEM) images. Experimental HRTEM images were simulated using the JEMS software with the following TEM parameters:

<table>
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**Figure S14** | **Typical HRTEM images at 200kV of mono and multilayer 2D-phosphane** viewed in the crystallographic projection along the $c$-axis ((110) zone axis corresponding to the edge-on view and slightly tilted ($17^\circ$) top view) in (a) – (b) and along the $b$-axis ((201) zone axis) in (c) – (d): HRTEM images are shown in (b) and (d). Fast Fourier Transforms of the white dashed areas highlighted in images (b) and (d) are shown in (a) and (c) respectively together with corresponding simulated images of the structure models depicted in blue. e Evolution of the number of monolayers along the cross line in the inset extracted from the High Angle Annular Dark Field (HAADF) contrast image (inset) taken at the edge of a thin flake.

**v) TEM Analysis and EELS measurements of oxidation.** Figure S15 displays the full core loss spectra recorded at 80 kV within key regions of the sample for TEM analysis shown in Figure 3 (main text). Different oxidation states of phosphorous are clearly identified by inspecting the P-
L2,3 edge on three different locations. The assignments of the peaks are based on comparison of the core shifts in X-ray photoelectron spectroscopy as given in Refs (3) and (4). The main sharp P-L2,3 edge at 130.2 eV is the main signature of the pristine P(black) structure\(^3\), whereas the weak peak at 136 eV is assigned to an oxidized state of P-L2,3. The oxidation state of this \(P_xO_y\) feature is close to that of \(P_2O_5\) based on similarity with the 2p photoemission of \(P_2O_5\) at 135eV.\(^4\) Correlated with the peak at 136 eV, the spectrum displays a small feature at 534 eV, corresponding to the O-K edge.

**Figure S15** | Core loss spectrum recorded at 80 kV with an energy resolution of 0.8 eV on a multilayer 2D-phosphane sample at P-L2,3 and O-K edges. Spectra (1), (3) and (4) correspond to regions near (1), (3) and (4) in Figure 3 (main text), respectively.
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Correlated with the peak at 136 eV, the spectrum displays a small feature at 534 eV, corresponding to the O-K edge.

Figure S15 | Core loss spectrum recorded at 80 kV with an energy resolution of 0.8 eV on a multilayer 2D-phosphane sample at P -L2,3 and O-K edges. Spectra (1), (3) and (4) correspond to regions near (1), (3) and (4) in Figure 3 (main text), respectively.

Figure S16 | HAADF image (a) and core loss images at 136 eV (b) and 534 eV (c), recorded at 80 kV with an energy resolution of 0.8 eV. The Pt-4 mark in (a) corresponds to the location Pt 3 of the EELS spectrum shown in Figures 4d-f of the main text.

Figure S17 | a) HAADF image and b) evolution of the number of layer (N) of monolayer 2D-phosphane along the cross-section shown in a. Note: the data were used in Figure 2 of the main text.
We have developed a phenomenological model based on Marcus-Gerischer theory (MGT) in order to simulate the photo-induced oxidation process in n-layer 2D-phosphane and its dependency with layer thickness.

Charge transfer doping (CT) reaction (CT) between 2D-phosphane and the environment is here assumed to take place through partial reaction steps involving the well-known oxygen-water redox couple that is naturally present in air. This redox reaction is given by:

$$\text{O}_2 + 4e^- + 4H^+ \leftrightarrow 2H_2O.$$  

It was previously established that such oxygen-water redox equilibrium reaction, which is pH dependent, induces charge transfer that can displace the Fermi level of a semiconductor, such as graphene, towards the Nerstian potential of an aqueous (aq) solution of oxygen. This reaction is driven by the potential difference between the two systems while the potential of the solution is fixed because there is an infinite reservoir of oxygen in air. In the case of graphene, it was previously shown that such CT reaction in air leads to p-doping since the graphene Fermi level has to move by more than 0.8 eV in order to equilibrate with the Nerstian potential of the solution. In the case of P(black), the driving force of the CT is significant because the Nerstian potential of the redox reaction at pH 6 is -5.3 V (i.e. -5.3 eV potential energy relative to the vacuum level) whereas the workfunction of intrinsic P(back) is only about 4.2 eV. However, the CT reaction induces in this case local oxidation of P atoms and etching of 2D-phosphane (see main text) rather than doping.

For completion, the oxygen/water redox reaction above involves at least 4 intermediate steps (i.e. a total of 4 electrons) and each step presents different kinetics and intermediate species. The first is an electron transfer from P(black) to the solvated oxygen acceptor state according to:

$$\text{O}_2 + e^- \leftrightarrow \text{O}_2^*.$$  

Because this reaction does not require neither $H^+$ nor $H_2O^*$, it is pH independent. Also, its reverse direction is not really favored since $\text{O}_2^*$ species are reactive intermediates against $\text{O}_2$ in the same conditions than in panels a and b, respectively.

Figure S18 | Color-coded HAADF image of the as-prepared flake in Figure 3 (main text) and repartition of oxygen by hyperspectral EFTEM on n-layers 2D-phosphane. a, HAADF image of the flake with color codes: Red: 1-2 layers, Orange: 3-4 layers; Yellow: 5-6; Lime Green: 7-8; Blue Cyan or Aqua: 9-10; Violet: 11-12; Purple: >13 layers. b, zone profile of the normalized signal in the rectangle region in panel a. TEM images of the flake recorded at 80 kV just after exfoliation in air and in dark conditions (c) and after an exposition to a bright lamp during 20 seconds (d). e-f EFTEM images extracted from the data cube at the oxygen K-edge (534 eV) in the same conditions than in panels a and b, respectively.
C. MARCUS-GERISCHER THEORY OF PHOTO-OXIDATION

We have developed a phenomenological model based on Marcus-Gerischer theory (MGT) in order to simulate the photo-induced oxidation process in $n$-layer 2D-phosphane and its dependency with layer thickness.

**C1 - Charge transfer doping**

Charge transfer reaction (CT) between 2D-phosphane and the environment is here assumed to take place through partial reaction steps involving the well-known oxygen-water redox couple that is naturally present in air. This redox reaction is given by:

$$ O_2(aq) + 4e^- + 4H^+ \rightleftharpoons 2H_2O. $$

It was previously established that such oxygen-water redox equilibrium reaction, which is pH dependent, induces charge transfer that can displace the Fermi level of a semiconductor, such as graphene, towards the Nerstian potential of an aqueous (aq) solution of oxygen\(^5\). This reaction is driven by the potential difference between the two systems while the potential of the solution is fixed because there is an infinite reservoir of oxygen in air. In the case of graphene, it was previously shown that such CT reaction in air leads to p-doping since the graphene Fermi level has to move by more than 0.8 eV in order to equilibrate with the Nerstian potential of the solution\(^6\). In the case of P(black), the driving force of the CT is significant because the Nerstian potential of the redox reaction at pH 6 is -5.3 V (i.e. -5.3 eV potential energy relative to the vacuum level) whereas the workfunction of intrinsic P(back) is only about 4.2 eV \(^7\). However, the CT reaction induces in this case local oxidation of P atoms and etching of 2D-phosphane (see main text) rather than doping.

**C2 - Rate limiting step**

For completion, the oxygen/water redox reaction above involves at least 4 intermediate steps (i.e. a total of 4 electrons) and each step presents different kinetics and intermediate species. The first is an electron transfer from P(black) to the solvated oxygen acceptor state according to:

$$ O_2(aq) + e^- \rightleftharpoons O_2^-(aq). $$

Because this reaction does not required neither $H^+$ nor $OH^-$, it is pH independent. Also, its reverse direction is not really favored since $O_2^-(aq)$ species are reactive intermediates against
P(black). In the MGT framework, this CT step is expected to be very slow because aqueous O\textsubscript{2} acceptor state is located at about -3.1 eV relative to vacuum\textsuperscript{6}, which is well above that of the P(black) band edges (See Figure S19). As a result of poor overlap, this CT step appears as the rate limiting step for the oxidation of P(black) in air. Two experimental facts described in the main text support this hypothesis: 1) CT rate as determined by Raman is very slow in the dark; 2) the photo-oxidation reaction is found to be independent of the pH of the solution, at least in the range between 5.8 and 7.8.

**C3 - Reaction kinetics based on MGT**

**i) General expression and considerations about energy levels.** To access the kinetics of the photo-induced CT reaction, we use the MGT describing the interaction of the solvent (water) with O\textsubscript{2(aq)} and O\textsubscript{2−(aq)}. Because of fast water rearrangements due the presence of the charge, the level fluctuates in energy over a range of ± 1 eV,\textsuperscript{8} which is expressed in the MGT using a total distribution (TD) function of the state that follows a Gaussian shape (See Figure S19). This CT rate is given by:

\[
D_{O_2}(E) = [O_2] \cdot b_o \exp \left(\frac{-(E-E_{F,redox}^0-\lambda)}{4kT\lambda}\right),
\]

where \([O_2]\) is the concentration of oxygen in water, \(E\) is the potential energy (in eV), \(E_{F,redox}^0\) is the electrochemical potential energy (or Fermi level of the solution), \(\lambda\) is the reorganization energy, and \(b_o\) is a normalizing parameter such that \(\int D_{O_2}(E)dE = [O_2]\). In principle, the CT kinetics may be related to the overlap between the density of states of the \(n\)-layer 2D-phosphane and the solution, but the levels in the solution are not equivalent, in a conventional sense, to that a band. That is, an electron cannot be transferred to aqueous oxygen through a simple physical process, such as band-to-band tunneling, because molecular rearrangements are taking place during the course of the reaction\textsuperscript{5}. It remains however possible, energetically, to transfer an electron from P(black) or \(n\)-layer 2D-phosphane with conduction electrons to the oxygen state because the energy levels are close.

Because \(E_{F,redox}^0 = -4.1\) eV for \(O_2(aq)/O_2^{-}(aq)\) and workfunction of P(back) is about 4.2 eV (bandgap, \(E_g=0.35\) eV), it appears clear in Figure S19 that intrinsic (undoped) P(black) should be
roughly stable in normal condition, which is consistent with experimental observations of a relatively good stability of the crystal in air, as reported by Bridgeman more than 100 years ago.

Figure S19 | Sketch of the densities of states (DOS) of aqueous oxygen acceptor and of n-layer 2D-phosphane, as predicted by the Marcus-Gerisher theory. On the left: DOS of mono-, bi-, tri-layer 2D-phosphane and bulk P(Black) extracted from Ref. 7 and 11. On the right: the energy diagram of the DOS of aqueous oxygen acceptor from Ref. 5 with the enlargement of the DOS due to solvent reorganization. The figure also illustrates by the blue arrows the proposed CT reaction induced by photo-excitation of n-layer 2D-phosphane.
**ii) Detail on the kinetics of charge transfer to bulk P(black).** The kinetic for the oxidation of the P(black) can be described by the following set of reactions. The overall reaction is:

$$\theta + O_{2(aq)} + h\nu \rightarrow \theta_{ox}. \quad (S3)$$

S3 can be subdivided into the following mechanism:

$$\theta + h\nu \rightarrow \theta^*, \quad (S4)$$

$$\theta^* \rightarrow \theta + \Gamma_x, \quad (S5)$$

$$\theta^* + O_{2(aq)} \rightarrow O_{2(aq)}^- + \theta + h^+, \quad (S6)$$

$$O_{2(aq)}^- + \theta + h^+ \rightarrow \theta_{ox}. \quad (S7)$$

In these equations, $\theta$ is the coverage of pristine P(black); $\theta^*$ is the coverage of excited P(black) by light – note that $\theta^*$ is also linked to the carrier concentration of photo-generated electrons, $\delta\eta$, at steady state because of the formation of electron-hole pairs; $\theta_{ox}$ is the coverage of oxidized P(black) in the form of $PO_2$; $h\nu$ is a photon count; $\Gamma_x$ regroups all decay channels leading to the relaxation of P(black) excited state to its ground state (phonon generation, fluorescence, etc.); $k_1, k_2, k_3, k_4$ are the rate constants.

Reaction S4 describes the direct photoexcitation of P(black). In this equation, we consider that electron-hole pairs are produced from the excitation and their relaxation towards the CB edge is very fast. Thus, carriers are generated and characterized by the energy of the band edges. Reaction S5 represents all the decay channels, radiative or not, of P(black) excited states. Driven by the CT to aqueous $O_2$, CT reaction S6 is responsible for the formation of the aqueous oxygen radial anion at the surface of P(black). This reaction is slow and assumed to be the limiting step with a rate constant, $k_3$. As detailed below, $k_3$ can be readily derived by the MGT. The last reaction S7 is a fast oxidation of P(black) by the oxygen anion oxidative specie or related intermediates, leading to etching.

Note that additional reactions are required in order to complete the reduction of $O_2$ towards $H_2O$ (i.e. a total of 4 electrons are involved in the complete water/oxygen redox reaction). However, our experiments indicate a high reactivity of $O_{2(aq)}^-$ intermediate species towards P(black) and thus any further electron transfer steps are neglected. To be noted, the reaction S6 and S7 are p-
doping and de-doping processes of P(black), respectively. Thus, these steps overall lead to no doping of P(black). Furthermore, \( O_{2}^{-}(aq) \) species can attack any pristine sites on the P(black) surface because the positive charges in reaction S6 is delocalized in the P(black).

To simplify the reaction kinetics, we assume that S4 and S5 are characterized by extremely fast kinetics compared to the CT processes in S6 and S7. Thus, these reactions can be considered as static, while solving S4 and S5 for the photo-stationary equilibrium situation, which sets the carrier population available for CT, as:

\[
\frac{d\theta^*}{dt} = k_1 \theta \cdot \hbar \nu - k_2 \cdot \theta^* = 0 \quad \text{(S8)}
\]

This yields:

\[
\theta^* = \frac{k_1}{k_2} \theta \cdot \hbar \nu \quad \text{(S9)}
\]

From this equation, an excess of electron in the conduction band at steady state, \( \delta \eta \), can be obtained for CT, corresponding to a coverage \( \theta^* \). This excess is therefore directly proportional to the photon flux and surface coverage \( \theta \). The concentration of thermally generated carriers is neglected in the actual process, which is justified by the significant bandgap of the material (of more than 0.35 eV in \( n \)-layer 2D-phosphane). This is consistent with the good stability of our samples in ambient conditions when kept in the dark.

One can develop further S9 for \( n \)-layer 2D-phosphane to get as a first approximation: \( \delta \eta = g_{opt} \tau_\eta = (J_{ph} A \sigma_{n,abs} \rho_A n \theta) \tau_\eta \), where \( g_{opt} \) is the optical generation, corresponding to \( J_{ph} A \sigma_{n,abs} \rho_A n \theta \), and \( \tau_\eta = \frac{1}{k_2} \) is the effective carrier lifetime (i.e. electron lifetime in the CB).

In this expression, \( J_{ph} \) is the laser flux, \( A \) the unit area, \( \sigma_{n,abs} \) is the absorption cross-section per atom, \( \rho_A \) is the phosphorus surface density, \( n \) is the number of layer. Note that for thicker layers, the light attenuation has to be included in \( g_{opt} \) using the following approximation: \( g_{opt} = J_{ph} A \theta (1 - \exp (-\sigma_{abs} \rho_A n)) \). Hence, the optical generation simply tends to \( J_{ph} A \) for bulk material where \( \theta \) is 1.

In the presence of the aqueous oxygen condensed at the surface of P(black), the electron transfers from the CB edge to the oxygen acceptor state of the solution proceeds according to reaction S6. This process generates aqueous superoxide anions, \( O_{2}^{-}(aq) \), that react spontaneously with the
surface atoms of n-layer 2D-phosphane and etch them in the process. We can then assume that
the oxidation reaction will be mainly limited by the S6 reaction step.

In the MGT framework, the electron transfer rate between the conduction band of P(black) and
the acceptor states of the solution, described by S6, is explicitly given by:

\[
\frac{d\tilde{O}_2^{aq}(t)}{dt} = \int_{-\infty}^{\infty} b_i \theta^* (1 - f(E)) D_{O_2}(E) dE. \quad (S10)
\]

Where \(D_{O_2}\) is given by S2, \(b_i\) regroups several prefactors related to the geometry of the molecular
system and \(f(E)\) is the Fermi-Dirac distribution. Assuming now that all electrons are distributed at
the minimum of the CB of a n-layer 2D-phosphane, \(E_{c,n}\), by a Dirac delta function, we obtain
after integrating:

\[
\frac{d\tilde{O}_2^{aq}(t)}{dt} = b_i \theta^* D_{O_2}(E_{c,n}), \quad (S11)
\]

or more explicitly using \(\delta\eta^\theta = \theta^*\) and equation S2:

\[
\frac{d\tilde{O}_2^{aq}(t)}{dt} = b_i b_o [O_2] \delta\eta \exp \left[ -\frac{(E_{c,n} - E_{F,redox}^0 - \lambda)^2}{4kT\lambda} \right]. \quad (S12)
\]

Because the rate equation for reaction S6 is: \(\frac{d\tilde{O}_2^{aq}(t)}{dt} = k_3 \theta^* [O_2]\), the reaction constant \(k_3\)
therefore become:

\[
k_3 = b_i b_o \exp \left[ -\frac{(E_{c,n} - E_{F,redox}^0 - \lambda)^2}{4kT\lambda} \right]. \quad (S13)
\]

Last, we can also write Equation S12 by taking into account that \(\frac{d\tilde{O}_2^{aq}(t)}{dt} = \frac{d\theta_{ox}}{dt} = -\frac{d\theta}{dt}\). By
renaming the variable \(b \equiv b_i b_o\), the oxidation rate can be formulated by the following kinetic
equation:

\[
\frac{d\theta}{dt} = -b \delta\eta [O_2] \exp \left[ -\frac{(E_{c,n} - E_{F,redox}^0 - \lambda)^2}{4kT\lambda} \right]. \quad (S14)
\]
The above expression can also be rewritten in terms of the energy gap of a \( n \)-layer 2D-phosphane, \( E_{g,n} \), assuming an intrinsic Fermi level, \( E_i \), \( i.e. \) in the middle of the gap. With the definitions above, we can develop more explicitly the expression for the oxidation rate of the P(black):

\[
\frac{d\theta}{dt} = -b(A\sigma_{abs}n_0) \cdot \theta f_{ph} [O_2] \cdot \exp \left( \frac{(E_{g,n}/2) + E_i - E_{F,red,ox} - \lambda}{4k_BT} \right).
\]  

(S15)

As discussed in the main text, the above expression describes well the observed behavior for the photo-oxidation of the P(black) and of \( n \)-layer 2D-phosphane. That is, the Raman intensity is proportional to the coverage \( \theta \), which then decays exponentially with time. The oxidation rate is also directly proportional to the photon flux, the \( O_2 \) concentration (or partial pressure) and more strikingly, as evidenced by TEM-EELS results, the rate is fastest for the thinnest \( n \)-layer 2D-phosphane. As a final note, the rate increases linearly with \( n \) and exponentially with the square of \( E_{g,n} \). As explain below, quantum confinement directly influences \( E_{g,n} \) and hence the kinetics.

C5 - On the consequences of electronic confinement on CT kinetics

The situation of \( n \)-layer 2D-phosphane is different than for bulk P(black) because electronic confinement leads to an enlargement of the band gap energy\(^{10,11}\). According to MGT, larger bandgaps should indeed improve the energy level alignment between the 2D-phosphane conduction band and the solvated oxygen acceptor state (see illustration in Figure S19). Hence, MGT predicts faster kinetics for electron transfer reaction toward the solution acceptor states (\( i.e. O_2(aq) \)) with decreasing thickness of the layer. In other words, the rate of transfer from the conduction band increases exponentially with the square of the bandgap energy, as indicated in Equation S15. Note that this is true up to the maximum level of the acceptor states, which is roughly -3.1eV. This situation is illustrated in Figure S19 by the relative length of the arrows in blue. Interestingly, as multilayer 2D-phosphane becomes thinner in some regions, etching is further promoted. The acceleration of the degradation for intermediate thicknesses and the formation of bumps for “bulk sample” is yet another consequence of the change in kinetics for that any disturbance of the local environment will lead to faster kinetics.

For intrinsic \( n \)-layer 2D-phosphane kept in the dark, the electron population in the conduction band is rather limited at room temperature and mainly given by the intrinsic carrier concentration.
This population decreases with increasing bandgap. This explains the relatively good stability of multilayer 2D-phosphane in the dark in ambient condition. As discussed in the main text, n-layer 2D-phosphane will generate when exposed to light a significant carrier population that is photo-generated by the process. The electrons and holes accumulate at the conduction and valence band edges and become available for transfer to the aqueous oxygen acceptor states.

REFERENCES


