MoS₂ pixel arrays for real-time photoluminescence imaging of redox molecules

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Measuring the behavior of redox-active molecules in space and time is crucial for understanding chemical and biological systems and for developing new technologies. Optical schemes are noninvasive and scalable, but usually have a slow response compared to electrical detection methods. Furthermore, many fluorescent molecules for redox detection degrade in brightness over long exposure times. Here, we show that the photoluminescence of "pixel" arrays of monolayer MoS₂ can image spatial and temporal changes in redox molecule concentration. Because of the strong dependence of MoS₂ photoluminescence on doping, changes in the local chemical potential substantially modulate the photoluminescence of MoS₂, with a sensitivity of 0.9 mV/√Hz on a 5 µm × 5 µm pixel, corresponding to better than parts-per-hundred changes in redox molecule concentration down to nanomolar concentrations at 100-ms frame rates. This provides a new strategy for visualizing chemical reactions and biomolecules with a two-dimensional material screen.

INTRODUCTION

Transition metal dichalcogenides (TMDs) such as MoS₂ are two-dimensional (2D) semiconductors with a bandgap in the visible portion of the electromagnetic spectrum. TMDs have received great interest since the discovery that a monolayer of MoS₂ is a direct bandgap semiconductor (1, 2). Since then, the PL of TMDs has been studied extensively and shown to respond to electrostatic gating (3, 4), chemical doping (5, 6), changes in pH (7), and defects (8, 9). However, only a few studies have exploited this sensitivity to use MoS₂ PL as a chemical or biological sensor. Early work on biological sensors used ion intercalation schemes to optically measure cell viability (10, 11). Researchers have also studied charge transfer processes between MoS₂ and a variety of electrolytes, observing charge transfer rates dependent on illumination intensity (12) and back-gate voltage (13).

One attractive application for TMDs, which has not been previously demonstrated, is the spatially resolved optical detection of redox conductors with a reasonable photoluminescence (PL) efficiency (1, 2). Since then, the PL of TMDs has been studied extensively and shown to respond to electrostatic gating (3, 4), chemical doping (5, 6), changes in pH (7), and defects (8, 9). However, only a few studies have exploited this sensitivity to use MoS₂ PL as a chemical or biological sensor. Early work on biological sensors used ion intercalation schemes to optically measure cell viability (10, 11). Researchers have also studied charge transfer processes between MoS₂ and a variety of electrolytes, observing charge transfer rates dependent on illumination intensity (12) and back-gate voltage (13).

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Fig. 1. MoS₂ PL response due to a change in [Fc⁺]/[Fc] ratio. (A) Bright-field transmitted light optical image of a MoS₂ pixel array consisting of 5 µm × 5 µm MoS₂ squares and Ti/Au contacted devices. The Pt/Ir electrode used to contact devices and oxidize the ferrocene molecules is shown in the middle of the image. (B) PL image of the same region in (A) excited by the 546-nm peak of a mercury lamp and imaged with a filter centered at 650 nm. The image shown is taken with a 2-s integration time. (C) Schematic of the charge transfer between ferrocene molecules and MoS₂. The red shade represents positively charged ferrocene molecules (ferrocenium). (D) PL of MoS₂ pixels varying the relative concentrations of ferrocene and ferrocenium.
molecules at the micrometer scale. Current approaches for spatially resolved redox molecule sensing include arrays of microelectrodes (14, 15), altered complementary metal-oxide-semiconductor (CMOS) camera detectors (16), ion-sensitive field-effect transistor arrays (17), and scanning electrochemical microscopy (SECM) (18). These techniques, particularly microelectrode arrays and SECM, can be used for diverse applications and are unlikely to be completely replaced by any optical techniques. They demonstrate high-speed detection and resolution at the few micrometer level. However, in certain circumstances, a completely wireless readout of chemical activity and molecular concentration is advantageous. Existing optical detection methods include scanned photocurrent (19), porous silicon (20), and surface plasmon (21, 22) techniques, and methods using fluorescent molecules and nanomaterials (23–25). Organic fluorescent molecules can be used to detect a wide variety of redox molecules with high spatial and temporal resolution but suffer from photobleaching (24, 25), leading to interest in using photoluminescent nanomaterials in chemical sensing applications.

In this work, we show that MoS2 pixel arrays are a powerful class of sensors for detecting redox-active molecules. Patterned arrays of MoS2 squares are used to measure changes in redox concentrations with micrometer-scale spatial resolution and at 10-ms temporal resolution. We can detect concentration changes on the order of few nanomolar concentrations, on par with the best electrical microelectrode detectors. These MoS2 pixels can be deployed in a wide variety of environments, from optical fibers to microfluidic systems, making them an attractive redox sensing platform for numerous applications.

RESULTS

The samples consist of photolithographically patterned MoS2 directly grown on fused silica substrates using metal-organic chemical vapor deposition (26). We examine two different geometries: MoS2 “pixel arrays” (Fig. 1A, left) consisting of small (2 μm × 2 μm or 5 μm × 5 μm) electrically floating squares, and MoS2 ionic liquid gate transistors (Fig. 1A, right) with Ti/Au contacts. We patterned MoS2 into pixels so that each pixel would be electrically isolated from all the others to measure the local chemical potential. For most of the measurements reported here, the samples were placed in a standard supporting electrolyte solution consisting of tetrabutylammonium hexafluorophosphate (Bu4NPF6) in acetonitrile. The redox couple ferrocene/ferrocenium was added as indicated. Similar results were obtained with other redox couples in aqueous environments. Details regarding the sample preparation process can be found in Materials and Methods and the Supplementary Materials.

Figure 1B shows the PL of MoS2 in a solution of Bu4NPF6 in acetonitrile. Both the pixels and the devices show bright PL. The observed internal quantum efficiency of ~10−4 is comparable to others reported in the literature (1, 27). Figure 1D shows the effect of the ferrocenium/ferrocene (Fc+/Fc) redox couple on the PL intensity for different Fc+/Fc ratios at a fixed 1 mM total concentration. The PL increases markedly with increasing concentration of ferrocenium. The Fc+ ions serve to extract electrons from MoS2, as shown schematically in Fig. 1C. This is consistent with the tuning of the PL in doped MoS2 observed previously as a function of a solid-state back-gate voltage (3, 4) and chemical doping with redox molecules (6). Additional increase of the PL could also occur due to defect screening by p-type molecules (28, 29). The devices thus operate as redox sensors, with order-of-magnitude changes in PL seen when changing the Ox/Red ratio.

The doping of electrically floating MoS2 pixels is akin to an open circuit potential (OCP) measurement. In an OCP measurement, the potential between a working electrode in solution and a reference electrode is measured in the absence of current flow, giving the electrochemical potential of the solution. In our case, changes in the PL of the MoS2 pixels indicate a change in the chemical potential of the solution near the MoS2 pixel, allowing spatially resolved chemical potentials to be optically read out. The mechanism can be understood by considering the
chemical potential of the solution $\mu_s$ set by the ferrocene/ferrocenium ratio. This chemical potential is given by the Nernst equation

$$\mu_s = eE_0 + k_B T \ln \left( \frac{[\text{Fc}^+]_0}{[\text{Fc}^-]} \right)$$

where $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $E_0$ is the standard reduction potential. As described in the equation above, an increase in the ferrocenium/ferrocene ratio results in an increase in the liquid potential. This change in chemical potential is followed by the MoS$_2$ Fermi level due to charge transfer between MoS$_2$ and ferrocene/ferrocenium. Thus, the shift in the chemical potential acts as an effective gate voltage on MoS$_2$ that changes the electron density and therefore the PL. This sensing mechanism is not sensitive to a single redox species but gives a readout of the local chemical potential of the solution.

To demonstrate this quantitatively, we compare the response of the pixels to measurements of the gated devices, shown schematically in Fig. 2A. Figure 2B shows both the PL and the two-probe in-plane conductance of the MoS$_2$ transistors as a function of the ionic liquid voltage ($V_{IL}$). As seen in the figure, the PL of the device decreases with the addition of electrons ($V_{IL} > 0$), and simultaneously, the device begins to conduct. For $V_{IL} < 0$ V, the electrons are depleted and the PL increases and then saturates when the Fermi level of MoS$_2$ is in the bandgap of the semiconductor.

The equivalence of these different ways of shifting the charge density is demonstrated in Fig. 2C, where the PL of the pixels as a function of the chemical potential is plotted on the same graph as the dependence of the PL of the transistor devices on gate voltage. We observe a one-to-one correspondence between the change in liquid potential determined according to Eq. 1 and the directly applied ionic liquid gate voltage, with no rescaling. The two curves overlay accurately, indicating that the PL of the MoS$_2$ pixels is set by the shift in the chemical potential of the solution with changing redox molecule concentration. A voltage pulse is applied to the microelectrode going from a voltage below to above the oxidation voltage for ferrocene, $V_{ox} = 0$ to 0.8 V. This fast voltage step results in the rapid oxidation of ferrocene to ferrocenium. A few milliseconds after the voltage pulse, we observe a large increase in the PL of the MoS$_2$ pixels around our electrode (Fig. 3A and movie S1, with a 3D plot showing the distribution of bright pixels shown in Fig. 3B). The cloud of Fc$^+$ diffuses outward from the microelectrode, lighting up the rest of the MoS$_2$ pixel array.

By following the size of the ferrocenium cloud as a function of time, we can directly measure its diffusion constant in the solution. For a localized source such as a microelectrode, the concentration of ferrocenium as a function of time ($t$) is expected to follow the form (30)

$$[\text{Fc}^+] = A \times \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right),$$

where erfc is the complementary error function, $x$ is the distance from the microelectrode, and $D$ is the diffusion constant of ferrocenium. By plotting pixel brightness as a function of $x$ for each frame and fitting every plot with the above equation (Fig. 3C), we obtain the radius $R$ of the ferrocenium cloud as a function of time. Figure 3D plots the radius $R^2$ of the ferrocenium cloud for simple diffusion. Linear fitting yields $D = (1.76 \pm 0.02) \times 10^{-9}$ m$^2$/s, which agrees with the values for...
Reynolds et al. increases with increasing area. The noise power spectra for all three sizes of MoS2 redox detectors. The left axis shows photons detected squared per hertz, and the right axis is converted to voltage via a MoS2 gate curve. All curves are taken at 10-ms exposure times. Power spectrum for a 2 μm × 2 μm pixel (A), a 5 μm × 5 μm pixel (B), and a 15 μm × 15 μm MoS2 region (C). The shot noise limit of our setup is shown by the dashed gray lines and corresponds to 1.5 mV/√Hz for (A), 0.6 mV/√Hz for (B), and 0.2 mV/√Hz for (C). The insets show the PL versus time graphs from which the power spectra were calculated.

The noise power spectra for (B), and 0.2 mV/√Hz for the 5 μm × 5 μm MoS2 pixel, and 0.5 mV/√Hz for the 15 μm × 15 μm MoS2 region. The voltage noise can be translated to an [Ox]/[Red] detection resolution through the Nernst equation. For a concentration ratio of ferrocenium to ferrocene (r = [Fc⁺]/[Fc]), the resolution is given by δv = GkT/2. This gives a redox detection resolution of δv = 0.03 Hz⁻¹/₂ or 10% at a 25-Hz bandwidth on a 5 μm × 5 μm pixel. This detection limit, which is independent of the initial concentration, is advantageous for measuring changes in redox molecule concentration in dilute solutions, as we demonstrate below.

We now compare MoS2 pixel redox sensors to the standard electrochemical method for measuring redox molecules, cyclic voltammetry (CV). We performed cyclic voltages sweeps at an ultramicroelectrode while monitoring the PL of nearby MoS2, shown schematically in Fig. 5A. These measurements were done at ferrocene concentrations ranging from 50 μM to 1 mM, as seen in Fig. 5B. Iw abruptly increases when the working electrode voltage overcomes the oxidation voltage for ferrocene at roughly the same values for each concentration of ferrocene. Similarly, we observe a sharp increase in PL intensity above the ferrocene oxidation potential, coinciding with the turn on in current for the CV measurements. However, these two measurements have a crucial difference: While the current at the microelectrode scales linearly with the initial concentration, the PL produces roughly the same response to sweeps in voltage down to the micromolar range of initial concentrations of ferrocene (Fig. 5B). Because the PL response is not specific to ferrocene, the lowest concentration sweep at 50 μM is limited only by the background concentration of any other redox molecules in the solution. MoS2 can be doped by any redox molecule that transfers charge with MoS2. PL and CV curves for a system with ruthenocene and a mixture of ferrocene and ruthenocene can be seen in the Supplementary Materials (fig. S3). We observe that the PL responds to increases in concentration of both ferrocenium and ruthenocenium.

The CV measurements and MoS2 PL measurements are related by the Nernst equation (Eq. 1). Assuming that the large initial ferrocene concentrations [Fc+] remains constant and the concentration of ferrocenium is proportional to the current to the working electrode (a valid assumption provided the electrochemical system is in steady state as defined in the Supplementary Materials), we can rewrite Eq. 1 as $\mu \propto k_B T I_m (I_{CV}/[Fc^+])$. Therefore, for the region of MoS2 doping where the PL intensity is linear with the electrochemical potential, we expect
that \( \text{PL} \propto k_B T \ln \left( \frac{I}{F C_0} \right) \). By plotting this change in potential versus \( \log \left( \frac{I}{F C_0} \right) \), the data should collapse onto the same curve independent of ferrocene concentration. This is what we observe (Fig. 5C). Our data are well fit by Eq. 1 with \( k_B T/e = (21 \pm 5) \) meV (with uncertainty in the conversion between PL and voltage constituting the largest source of error), indicating a simple relationship between standard current-based detection methods for calculating concentration and our method using MoS\(_2\) PL.

Since the signal for MoS\(_2\) PL detection of molecules is independent of absolute concentration and depends instead on the ratio of oxidized-to-reduced species, it provides a method for detecting redox molecules that scales favorably down to low concentrations. To test the detection limits of our system, we performed simultaneous CV sweeps and PL measurements of MoS\(_2\) pixels at lower concentrations of ferrocene, shown in Fig. 5D. Although the current at our microelectrode falls below the detection limit of our setup for concentrations under 10 \( \mu \)M, the PL of MoS\(_2\) attains the same value as a function of voltage for 10 and 1 \( \mu \)M concentrations. The response begins to shift at 100 and 10 nM concentrations, perhaps due to comparable concentrations of contaminant redox molecules, but still reaches the same peak PL intensity. The low detection limit of sub–10 nM concentrations using MoS\(_2\) PL improves upon ultramicroelectrode detection limits for concentration detection, which are reported to be at best around 50 nM.

Having explored the operation of the pixel arrays for redox sensing, we illustrate their use in a variety of situations. Figure 6 (A and B) shows a MoS\(_2\) pixel array deployed in a polydimethylsiloxane (PDMS)
A microfluidic channel to measure the spatial distribution of the oxidation state of redox active molecules. A syringe pump connected to the channel supplies pressure-driven (laminar) flow, while a platinum surface electrode on chip can be used to perform redox chemistry in the channel. A short pulse applied to the surface electrode oxidizes ferrocene in the channel to ferrocenium, which is carried to the right by the flow. The resultant PL response of the MoS₂ pixel array is shown in Fig. 6B and movie S2, allowing the direct tracking of the oxidized molecules in real time with micrometer and millisecond spatial and temporal resolution. Similar results for electroosmotic flow are shown in the Supplementary Materials.

These pixel arrays can be transferred to almost any substrate. Figure 6C shows a MoS₂ pixel array on an optical fiber where the light through the fiber is used to excite the pixels. Figure 6D shows a measurement of the PL, as a probe nearby periodically oxidizes ferrocenium.

DISCUSSION
This work demonstrates a previously unknown class of 2D fluorescent sensors for the detection of redox-active species. The sensor is shot noise limited, with a sensitivity of 10% in a 30-Hz bandwidth at a 5 μm × 5 μm pixel and detection limits down to nanomolar concentrations. Improvements to the PL efficiency could increase this sensitivity by another one to two orders of magnitude. Future work could also include functionalization of MoS₂ for specific molecular detection, following approaches used for other photoluminescent nanomaterials. The fast, all-optical detection of chemical potentials and ionic densities using the PL of a 2D material has great potential for monitoring various chemical and biological systems, such as hydrogen evolution reactions and neurochemical activity (the Supplementary Materials present initial measurements of dopamine). Being flexible, chemical inert, and easily transferrable, MoS₂ provides a local redox sensing method that can be easily incorporated into a broad range of environments and systems.

MATERIALS AND METHODS
MoS₂ growth and device fabrication
The MoS₂ sheets were grown by metal-organic chemical vapor deposition on 1” fused silica wafers as described in (26). After initial PL and atomic force microscopy characterizations (fig. S1), we defined Ti/Au (5/50 nm) electrodes and alignment markers using conventional optical lithography and metal evaporation methods. The MoS₂ structures (pixels and device channels) were defined by a final optical lithography step followed by reactive ion etching (SF₆:O₂ 5:1 ratio at 20 W). To increase the PL quantum efficiency in our films, we treated our final structures with bis(trifluoromethane) sulfonimide following the procedures detailed in (27).

Experimental setup
The devices were measured using a probe station with automated micromanipulators (Sensapex). The samples were mounted with the MoS₂ side pointing up on an inverted microscope and imaged with a water immersion 60× objective with numerical aperture 1.25 and an Andor EMCCD.

The PL measurements were made using a mercury arc lamp combined with a 550-nm band-pass filter [40-nm full width at half maximum (FWHM), Thorlabs] and a dichroic mirror (552-nm...
long pass, Semrock) as our incident light beam. The reflected light is partially filtered by the dichroic beamsplitter and further selected using a 650-nm band-pass filter (40-nm FWHM, Thorlabs), which includes the A-exciton peak at room temperature (~660 nm). For the electrochemical measurements, we used a Pt wire as our quasi-reference electrode and Pt/Ir microelectrode probes (Microprobes for Life Sciences) with ~1 megaohm impedance at 1 kHz to the liquid as our working electrode.

**Electrolyte and ferrocene solution preparation**
The electrolyte solution for all the measurements presented consisted of 100 mM Bu4NPF6 (Sigma-Aldrich) in acetonitrile. After the electrolyte preparation, the desired amount of ferrocene (Sigma-Aldrich) was mixed to obtain the concentrations ranging from 1 nM to 100 mM used in our work.

The desired solution was then pipetted onto the fused silica chips containing the MoS2 structures, which sat on an inverted microscope. The liquid was contained by a PDMS ring (~2 mm thick), which sealed onto the wafer. For the measurements with increasing ferrocene concentration, we started with the lowest concentration and increased it by pipetting away the lower concentration and flushing the liquid with the higher concentration solution. If a series of measurements were required, the samples were flushed in acetonitrile several times to remove any adsorbed ferrocene molecules.

**REFERENCES AND NOTES**
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