MoS_2 Pixel Sensors for Optical Detection of Redox Molecules

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Primary CNF Tools Used: Autostep i-line, ABM contact aligner, SC4500 evaporator, Oxford 81 etcher, VersaLine etcher

Abstract:

Spatially-resolved detection of redox molecules in solution is important for understanding chemical and biological systems. Optical detection is advantageously wire-free and easily multiplexed. We demonstrate that monolayer molybdenum disulfide (MoS_2) is a fast, sensitive, optical sensor for redox molecules.

Summary of Research:

Redox molecule detection has applications from detection of neurotransmitters in the brain to trace chemical detection in water samples. Traditional techniques, such as cyclic voltammetry, provide sensitive detection at a single electrode, but do not spatially resolve the variation in redox concentration. More advanced approaches including multiplexed electrode arrays [1,2] and numerous optical detection techniques [3-6] allow researchers to image redox molecules.

We demonstrate a wireless, optical approach for fast, sensitive redox imaging using a flexible, transferrable monolayer of MoS_2. MoS_2 photoluminesces at about 650 nm [7], with an intensity that increases as the concentration of electrons on the MoS_2 decreases, as shown by back-gating [8] and chemical doping [9].

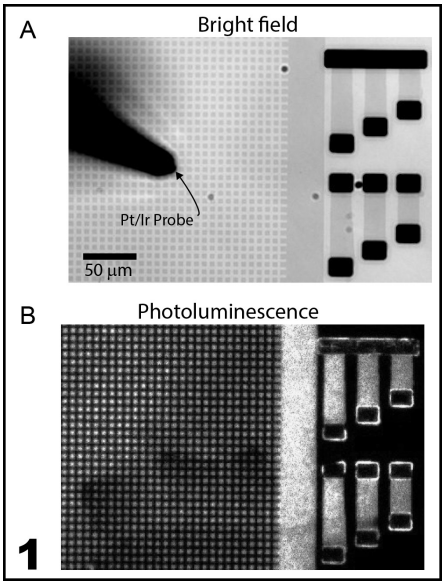
We use the doping dependence of MoS_2 photoluminescence (PL) to detect ferrocene/ferrocenium as a test redox couple. Metal-organic chemical vapor deposition MoS_2 samples [10], grown by Prof. Park's group, are patterned with a two-step fabrication process. First, we pattern contact pads on the MoS_2 with electron-beam evaporation. Second, we etch away the MoS_2 to define our device and pixel geometries, which are shown in Figure 1.

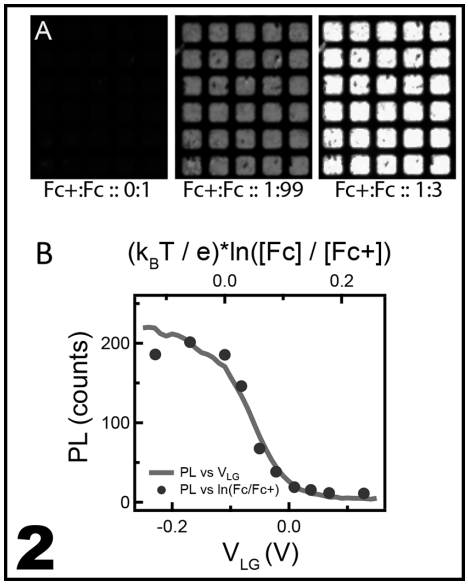
We performed two experiments to demonstrate that our MoS_2 pixel sensors measure the chemical potential of the solution. First, with a fixed total concentration of ferrocene/ferrocenium, we varied the ratio of the concentration of ferrocenium (Fc+) to ferrocene (Fc) in our solution while monitoring the PL of the MoS_2 (Figure 2A). The MoS_2 shows a marked increase in PL as Fc+/Fc increases. Second, in a solution without any ferrocene or ferrocenium, we apply a potential to the solution (denoted V_{LG} for liquid gate voltage) while grounding a contacted MoS_2 device. The PL is high at negative values for V_{LG}, but decreases as V_{LG} is swept to positive values (Figure 2B, red curve). We compare the PL *versus* liquid gate voltage to PL *versus* change in chemical potential, where the change in chemical potential of the solution is given by

$$\Delta\mu = \frac{k_B T}{e} \ln \frac{[Fc]}{[Fc+]},$$

according to the Nernst equation (Figure 2B, blue dots). The good agreement between the two curves indicates that the PL of electrically floating pixels is set by the chemical potential of the solution.

Having characterized the MoS_2 sensors, we measure diffusion to demonstrate their speed and spatial resolution. We apply a voltage pulse to a microelectrode positioned above our MoS_2 pixel array in a solution of 1 mM ferrocene. The pulse oxidizes ferrocene to ferrocenium, which diffuses away from the probe tip, creating a spreading ferrocenium concentration that is imaged by the MoS_2 pixels (Figure 3). From these data, we extract a ferrocenium diffusion constant of about 1.8×10^{-9} m^2/s, matching previous measurements [11].





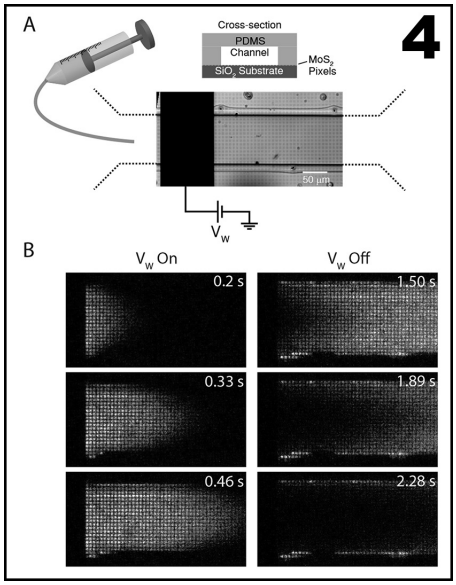


Figure 1, left: *A, Bright-field and B, PL (549 nm excitation, 650 emission) images of MoS_2 pixels and devices.* ***Figure 2, middle:*** *A, PL images of MoS_2 with varied ferrocenium/ferrocene ratios, showing increased PL with increased ferrocene concentration. B, PL versus liquid gate voltage for grounded device (red line) and versus solution chemical potential (blue dots), showing that MoS_2 sensors are Nernstian.* **Figure 4, right:** *A, Schematic and bright-field image showing PDMS microfluidic channel placed over MoS_2 pixel array. A pulse on the surface electrode oxidizes ferrocene to ferrocenium while a syringe pump flows the solution through the channel. B, MoS_2 PL imaging flow of ferrocene in the channel.*

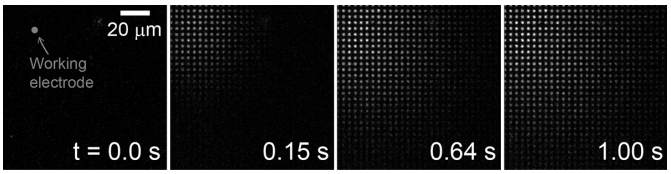


Figure 3: Frames from PL video imaging diffusion of ferrocenium away from a microelectrode after its potential is pulsed to 0.8 V versus the solution potential.

Finally, we use these sensors to image the flow of redox molecules in microfluidic channels. We mold polydimethylsiloxane (PDMS) microfluidic channels using silicon wafer masters patterned with the Plasma-Therm deep silicon etcher and place them over MoS_2 pixel arrays with platinum surface electrodes (Figure 4A). While flowing a ferrocene solution through the channel, we applied voltage pulses to the surface electrodes to oxidize ferrocene to ferrocenium and image laminar flow of the solution in MoS_2 PL (Figure 4B). These experiments show that MoS_2 can be used for real-time, spatially resolved imaging of redox molecules. The sensor could be improved by increasing the quantum efficiency of the MoS_2 PL in solution. In the future, these sensors could find applications in biological sensing experiments, e.g. spatially resolved detection of dopamine efflux from neurons.

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