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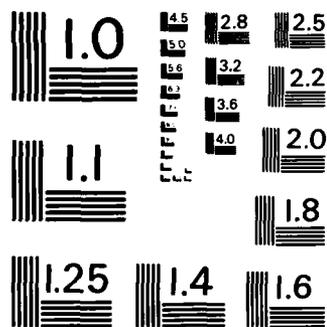
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Photoluminescent Response of Palladium-Cadmium Sulfide  
and Palladium-Graded Cadmium Sulfoselenide Schottky Diodes  
to Molecular Hydrogen

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The bulk photoluminescence (PL) of Schottky diodes constructed from Pd and n-type CdS (Pd-CdS) and from n-type, graded CdS <sub>x</sub> Se <sub>1-x</sub> (0 ≤ x ≤ 1; x = 1 at surface) (Pd-CdS <sub>x</sub> Se <sub>1-x</sub> ) is sensitive to molecular H <sub>2</sub> . For the Pd-CdS diode, exposure to H <sub>2</sub> (3:1, N <sub>2</sub> :H <sub>2</sub> mixture) significantly enhances the PL intensity of edge emission (λ <sub>max</sub> ≈ 510 nm) relative to the intensity in air; using a dead-layer model, the corresponding reductions in depletion width and Schottky barrier height can be estimated. For the Pd-CdS <sub>x</sub> Se <sub>1-x</sub> diode, H <sub>2</sub> changes the		

spectral distribution; PL from this material, color-coded to spatially resolve  $e^-h^+$  pair recombination, indicates the depth over which the electric field is reduced in the semiconductor. These phenomena demonstrate optically-coupled chemical sensing of hydrogen.

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## INTRODUCTION

The bulk photoluminescence (PL) of semiconductors has proven to be a useful probe of Schottky barrier characteristics in both semiconductor/metal diodes<sup>1</sup> and photoelectrochemical cells (PEC's).<sup>2</sup> In particular, the electric field in the semiconductor can be estimated from PL intensity using a dead-layer model: Electron-hole ( $e^-h^+$ ) pairs formed within a distance from the interface on the order of the depletion width do not contribute to PL. While the importance of surface properties on bulk PL has been described<sup>3,4</sup>, their interrelationship has not been examined experimentally in detail.

In choosing a system for such studies, our interest was drawn to Schottky diodes constructed with Pd because of the known sensitivity of their current-voltage (i-V) properties to gaseous  $H_2$ .<sup>5-8</sup> In general, Schottky barriers resulting from junctions of Pd with a variety of n-type semiconductors decreased upon exposure of the diode to  $H_2$ , reflecting diminution of the Pd work function by the gas.<sup>9</sup> The effect is sufficiently sensitive to  $H_2$  concentration that Pd-CdS<sup>5</sup> and Pd-TiO<sub>2</sub><sup>6</sup> Schottky diodes have been proposed as  $H_2$  detectors. Variation in Schottky barrier height with  $H_2$  appears to also strongly influence the efficiency with which metal-coated semiconductor electrodes evolve  $H_2$  in PEC's.<sup>10</sup>

We report herein that PL intensity from Pd-CdS Schottky diodes is substantially perturbed by exposure of the diode to  $H_2$ . Moreover, the PL properties are consistent with a dead-layer model, allowing calculation of the variation in electric field thickness with exposure to  $H_2$ . Schottky diodes constructed from Pd and a graded  $CdS_xSe_{1-x}$  ( $0 \leq x \leq 1$ ;  $x=1$  at surface) semiconductor<sup>11,12</sup> ( $Pd-CdS_xSe_{1-x}$ ) evince a change in spectral distribution upon exposure to  $H_2$ ; the color-coded nature of the light emitted from this semiconductor can be used to map the effective electric field in this solid and its perturbation by  $H_2$ . Besides illustrating the coupling of surface interactions to bulk PL, these studies demonstrate the feasibility of constructing optically-coupled chemical sensors.

EXPERIMENTAL SECTION

Samples of n-type, single-crystal, CdS and CdSe c-plates (1-mm thickness; ~2 ohm-cm resistivity) were purchased from Cleveland Crystals, Inc. and cut into pieces of ~0.25-cm<sup>2</sup> area. Graded samples of n-CdS<sub>x</sub>Se<sub>1-x</sub> (0 ≤ x ≤ 1) where the graded zone had a thickness of ~1.0 μm were prepared by vapor-phase diffusion of S into CdSe and characterized as described previously.<sup>12</sup> Prior to Pd deposition on its 0001 Cd-rich face, CdS was etched in Br<sub>2</sub>/MeOH (1:10 v/v); the graded CdS<sub>x</sub>Se<sub>1-x</sub> samples were not etched owing to the thinness of the graded layer.

Deposition utilized Pd foil (50x50x0.1 mm; >99.997% metallic purity; Aesar Co., Seabrook, NH) and a SPI Super Sputter apparatus. Sputtering was conducted at 2x10<sup>-4</sup> torr Ar pressure and 60-μA beam current for ~45 s; a parallel deposition onto Pt foil was used in conjunction with electrochemical stripping (0.75 V vs. SCE in 1M HCl aqueous electrolyte) to estimate the Pd layer thickness to be ~100 Å.

After deposition, electrical contact was made to the translucent Pd layer with Ag epoxy and to the back surface with Ga/In eutectic and Ag epoxy; Cu wires were connected to the Ag epoxy and current-voltage properties obtained with a PAR Model 173 potentiostat and Model 175 programmer.

PL spectra were recorded using 457.9- and 488.0-nm excitation from a CR-12 Ar<sup>+</sup> laser and an Aminco-Bowman spectrometer equipped with a Hamamatsu R446S PMT. The sample was enclosed in a cell which permitted dry N<sub>2</sub>, a 3:1 N<sub>2</sub>:H<sub>2</sub> mixture (Air Products tank of H<sub>2</sub> mixed with in-house N<sub>2</sub>), or air to bathe the sample; flow rates of ~0.5 l/min were employed. Optical properties of the Pd film were examined by depositing the metal on a microscope slide; transmission and reflectivity of 457.9-, 488.0-, and 514.5-nm light were measured in air and the N<sub>2</sub>/H<sub>2</sub> medium.

The PL spectrum from a Pd-CdS sample in air, illuminated through the metal with 457.9-nm ultraband gap ( $E_g \sim 2.4$  eV) light, is characterized by band edge emission at  $\sim 510$  nm,<sup>13</sup> as shown in Fig. 1. When a 3:1 mixture of  $N_2:H_2$  is passed over the sample, Figure 1 reveals that the PL intensity is enhanced by approximately 70%; the enhancement occurs over  $\sim 30$  s with the  $\sim 100\text{-\AA}$ -thick Pd layer. PL enhancement requires the presence of Pd but does not appear to derive from changes in the metal's optical properties: optical transmission and reflectivity of the metal film, deposited on a microscope slide, were insensitive to the presence of  $H_2$ . After flushing the sample cell with  $N_2$  and then with air, the PL intensity returns to its original value. This effect is reversible over at least 10 cycles. If more penetrating 488.0-nm light is used for excitation, the PL intensity is augmented by  $\sim 40\%$  with exposure to  $H_2$ . From current-voltage data, the Pd-CdS structure exhibits typical diode behavior in air and in the  $N_2/H_2$  medium.

These spectral changes are consistent with a reduction in Schottky barrier height resulting from the dissolution of  $H_2$  in Pd, a well-studied phenomenon.<sup>5-10</sup> Qualitatively, the PL intensity is expected to rise because the smaller electric field in the semiconductor allows a larger fraction of  $e^-h^+$  pairs to radiatively recombine. By regarding the region supporting the electric field as being completely nonemissive, i.e., a dead layer, a quantitative expression for relative PL intensity can be obtained, eq. (1); this treatment assumes that the CdS surface recombination velocity in the diode is either very large or insensitive to  $H_2$ .<sup>2,3</sup> In eq. (1),  $\phi_{H_2}$  and  $\phi_{air}$  are the radiative quantum yields in  $H_2$  and

$$\frac{\phi_{air}}{\phi_{H_2}} = \exp(-\alpha' \Delta D) \quad (1)$$

in air;  $\Delta D$  is the difference in dead-layer thickness between the two media; and  $\alpha' = (\alpha + \beta)$  with  $\alpha$  and  $\beta$  the solid's absorptivities for the exciting and emitted light, respectively. For CdS,  $\alpha$  for  $E_{\parallel c}$  polarized light is  $6 \times 10^4$  and  $\sim (9-10) \times 10^4$   $\text{cm}^{-1}$  for 488.0- and 457.9-nm light, respectively;  $\beta$  is  $7 \times 10^3$   $\text{cm}^{-1}$  at 510 nm.<sup>14</sup>

The PL enhancements seen for the two excitation wavelengths employed give a consistent value for  $\Delta D$  of  $\sim 500\text{-}600 \text{ \AA}$ . This value for the contraction of the electric field upon exposure to  $\text{H}_2$  can be used to calculate a reduction in Schottky barrier height of the initial height is known. Literature estimates for the Pd-CdS barrier height in air range from  $\sim 0.5\text{-}0.8 \text{ eV}$ ; <sup>5,7</sup> our  $i\text{-}V$  curves yield an estimated height of  $0.6 \text{ eV}$ . The depletion width  $W$  is related to barrier height  $qV$  by eq. (2), where  $\epsilon_0$  is the permittivity of free space,  $q$  is the electronic

$$W = \sqrt{\frac{2\epsilon\epsilon_0V}{q N_D}} \quad (2)$$

charge, and  $\epsilon$  and  $N_D$  are the semiconductor's dielectric constant and charge carrier density; for our samples,  $\epsilon$  and  $N_D$  are  $\sim 10$  and  $9 \times 10^{15} \text{ cm}^{-3}$ , respectively. <sup>15</sup> Substitution into eq. (2), equating  $D$  with  $W$ , leads to an estimated decline in barrier height of  $0.2 \text{ eV}$ . Literature values vary from  $\sim 0.5 \text{ eV}$  <sup>5</sup> to  $\sim 0.2 \text{ eV}$  (extrapolated). <sup>7</sup> The range of values likely reflects variations in sample preparation. <sup>16</sup>

A complementary system with  $\text{H}_2$ -sensitive PL is the Pd-CdS<sub>x</sub>Se<sub>1-x</sub> Schottky diode. The PL spectrum in air is shown in Fig. 2 and consists of edge emission from all of the CdS<sub>x</sub>Se<sub>1-x</sub> compositions which comprise the  $\sim 1.0\text{-}\mu\text{m}$ -thick graded zone, from CdS at the surface to the CdSe ( $E_g \sim 1.7 \text{ eV}$ ;  $\lambda_{\text{max}} \sim 720 \text{ nm}$ ) substrate. <sup>12</sup> A linear correlation exists between composition  $x$  and the emission band maximum, eq. (3). <sup>13</sup> In conjunction with AES/Ar<sup>+</sup> sputter etch data, eq. (3) provides

$$\lambda_{\text{max}}(\text{nm}) = 718 - 210 x \quad (3)$$

a map of radiative recombination in the solid: The PL is color-coded to indicate the depth from the surface at which  $e^-h^+$  pair recombination occurs. Perturbation of PL by applied potential reflects changes in the effective electric field

(EEF) in the solid<sup>11,12</sup>; we use the term "EEF" to reflect the fact that the electric field of this solid is complex and contains contributions, e.g., from band-edge gradients, in addition to the field arising from the Schottky barrier.

Exposure of a Pd-CdS<sub>x</sub>Se<sub>1-x</sub> diode to H<sub>2</sub> results in asymmetric enhancement of as much as 50% in the blue end of the PL spectrum, Fig. 2; the effect corresponds to a modest color change. The material has diode i-V characteristics in both environments. Qualitatively, the PL enhancement at shorter wavelengths indicates a reduction in the EEF in the near-surface region of the semiconductor, since it is the near-surface, S-rich compositions which give rise to the emission. A more quantitative estimate of the affected region is afforded by the cessation of spectral changes for  $\lambda \geq 600$  nm. From eq. (3) and AES/Ar<sup>+</sup> sputter etch data, exposure to H<sub>2</sub> influences the EEF to a depth of  $\sim 0.1 \mu\text{m}$  (1000 Å) from the surface.

In summary, bulk PL from Pd-CdS and Pd-CdS<sub>x</sub>Se<sub>1-x</sub> Schottky diodes provides a sensitive probe of changes in the electric field of the semiconductors resulting from a surface interaction with H<sub>2</sub>. The ability to transform molecular surface interactions into a change in bulk PL intensity (Pd-CdS) or color (Pd-CdS<sub>x</sub>Se<sub>1-x</sub>) could have applications to the design of optically-coupled chemical sensors. Further experiments designed to couple analyte sensitivity to PL are underway in our laboratories.

Acknowledgment. We are grateful to the Office of Naval Research, the Army Research Office, and the 3M Company for generous support of this research. Mr. R. K. Noll and Dr. J. Jacobs are thanked for their assistance with the Pd deposition process. Dr. Nils Blom is acknowledged for experimental assistance and helpful discussions.

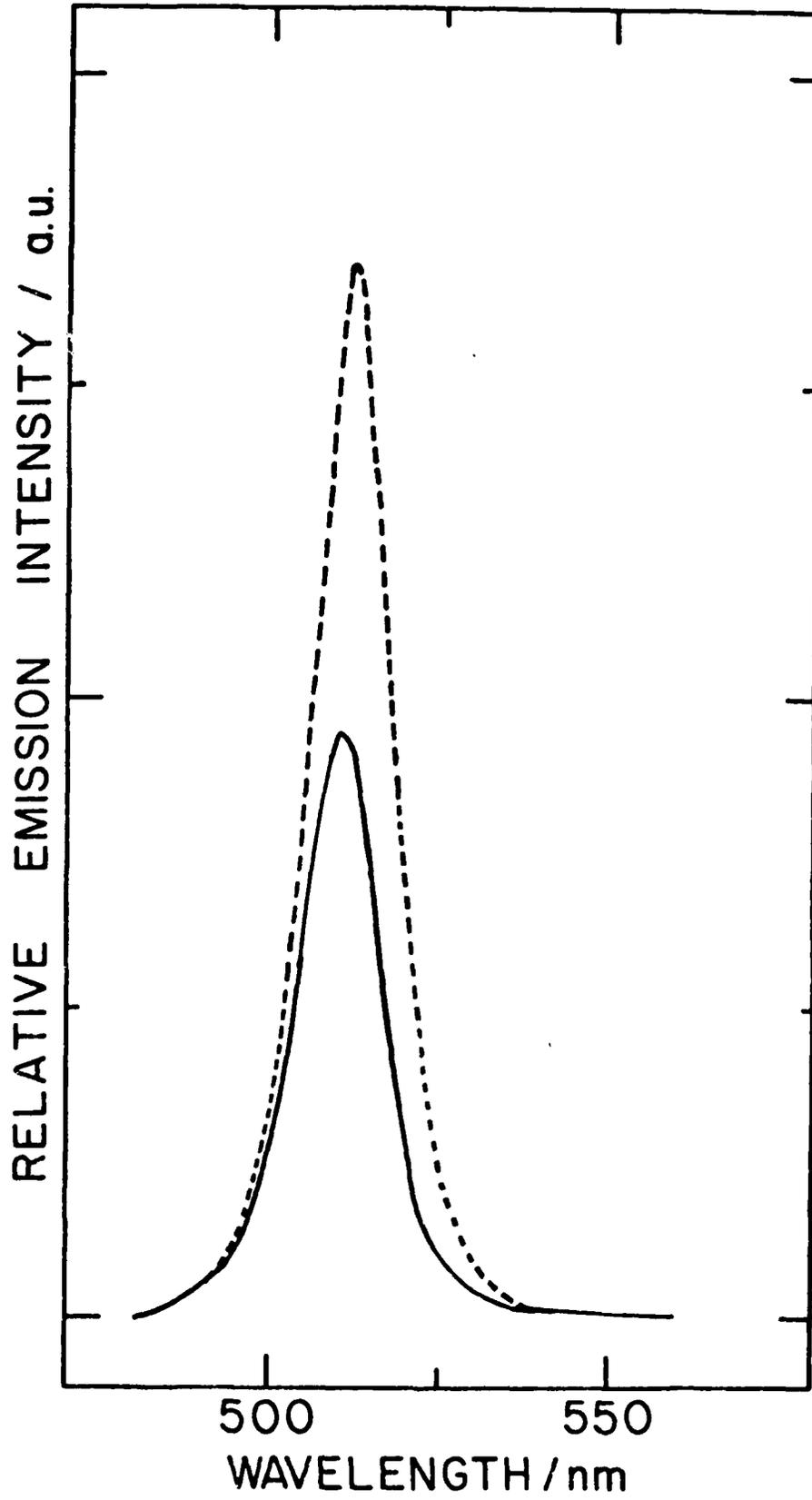
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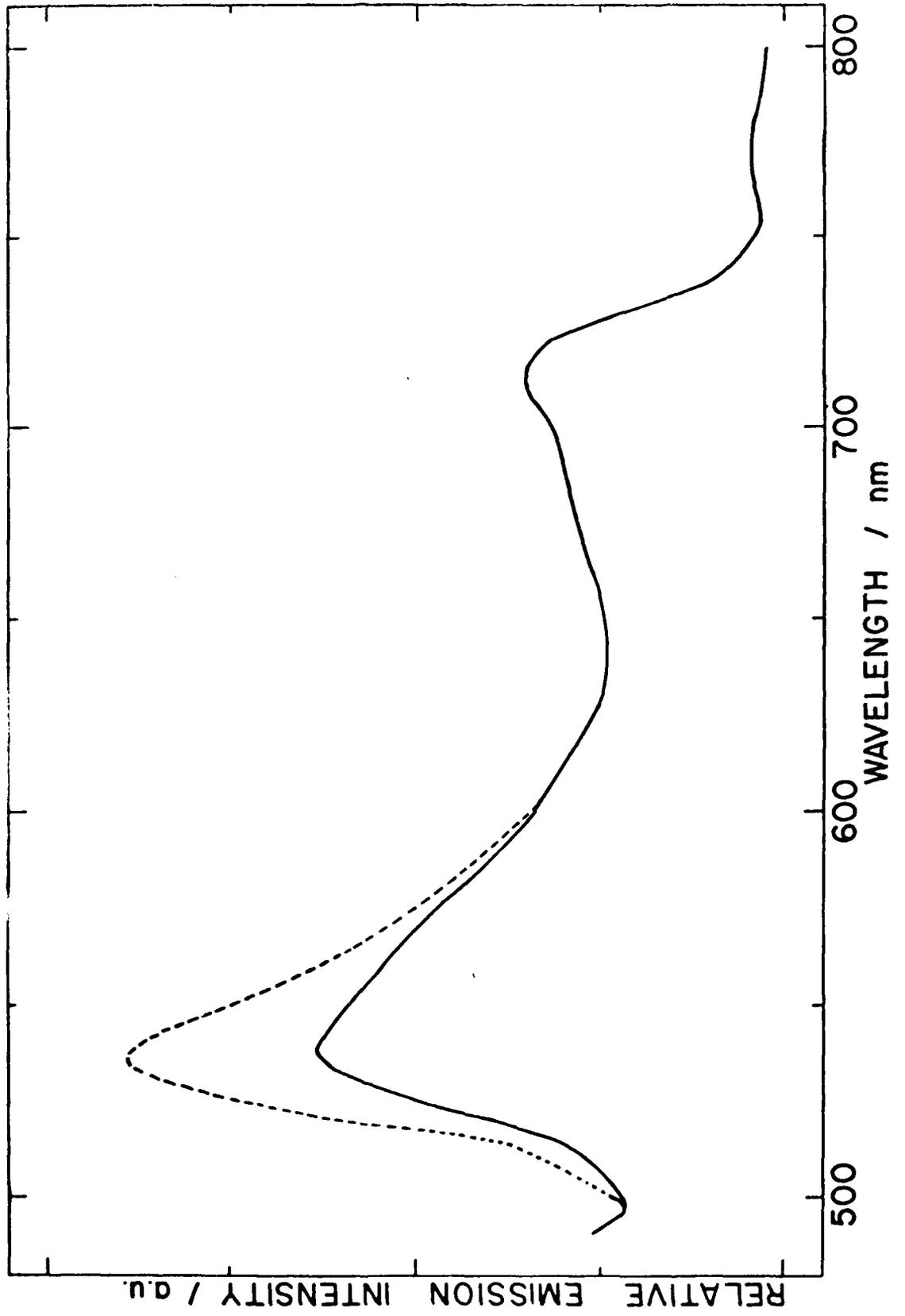
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## Figure Captions

Figure 1. Uncorrected PL spectra of a Pd-CdS Schottky diode in air (solid line) and in a 3:1, N<sub>2</sub>:H<sub>2</sub> atmosphere (dashed line). The sample was excited with the same intensity ( $\sim 40$  mW/cm<sup>2</sup>) of 457.9-nm light in both experiments, using an identical sample-detection optics geometry.

Figure 2. Uncorrected PL spectra of a Pd-CdS<sub>x</sub>Se<sub>1-x</sub> Schottky diode in air (solid line) and in a 3:1, N<sub>2</sub>:H<sub>2</sub> atmosphere (dashed line). The sample was excited with the same intensity ( $\sim 40$  mW/cm<sup>2</sup>) of 457.9-nm light in both experiments, using an identical sample-detection optics geometry.





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