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Imprinted Poly(acrylic acid) Films on Cadmium Selenide. A Composite Sensor Structure that Couples Selective Amine Binding with Semiconductor Substrate Photoluminescence

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Molecularly imprinted films of poly(acrylic acid) (PAA) have been coated onto n-CdSe in order to make the band-edge photoluminescence (PL) of the semiconductor respond selectively to the imprinting analyte. This strategy has been implemented using PAA films deposited in the presence of ammonia and trimethylamine analytes. PAA films have been characterized by IR spectroscopy, which indicates that binding of either analyte nearly reversibly deprotonates the polymer carboxylic acid groups. PL measurements suggest that the imprinted PAA coatings serve as sieves for selective surface binding: In contrast to the bare CdSe surface, which responds both to ammonia and trimethylamine with reversible enhancements in PL intensity, CdSe coated with ammonia-imprinted PAA (AI-PAA) films exhibits reversible PL changes toward ammonia but no response to trimethylamine. The PL changes for the AI-PAA films can be fit to a dead-layer model that indicates that ammonia binding reduces the CdSe depletion width by ~ 100 Å, an effect comparable to that seen for the bare surface. Binding constants of $\sim 10^3$ M⁻¹, estimated using the Langmuir adsorption isotherm model, are similar for adsorption of ammonia onto bare and AI-PAA-coated CdSe surfaces. Coating the CdSe substrate with trimethylamine-imprinted PAA (TI-PAA) films leads to PL responses to both ammonia and trimethylamine, presumably reflecting larger imprint pores that are less sterically demanding. Implications for chemical sensing using these composite structures are discussed.

Introduction

The band-edge photoluminescence (PL) of n-CdSe has been shown to be a useful tool for monitoring adsorption of a wide variety of solution and gas-phase analytes onto the semiconductor's surface.^{1,2} From these studies, a "PL litmus test" has been identified: Typically, Lewis acid adsorbates quench PL intensity, and Lewis bases enhance it relative to a reference ambient. The direction of the PL response appears to reflect adsorbate-induced changes in the semiconductor's depletion width and can be modeled by treating a near-surface region of this approximate thickness as nonemissive (dead-layer model).

A drawback of this sensing strategy is lack of selectivity. Typically, the semiconductor responds similarly to molecules bearing a common functional group, precluding its use for distinguishing among functionally related species. For example, we have found that gaseous ammonia and mono-, di-, and trimethylamine all yield PL enhancements when adsorbed onto the bare surface

of CdSe, with the magnitude of the response following the order $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$.³ A promising approach for imparting selectivity is to coat the semiconductor with a transducing film. In this way, the optical properties of the semiconductor are coupled to the chemical selectivity of the overlying (transducing) film. Reaction of the film with the target family of analytes has been shown to affect the PL of the underlying semiconductor.^{4–8}

It occurred to us that films of imprinted polymers might also afford a strategy for introducing selectivity to the CdSe surface. As depicted in Figure 1, molecularly imprinted polymer (MIP) films offer shape, size, and chemical selectivity, similar to recognition functions commonly found in nature, and have attracted considerable interest for chemical sensor applications.^{9–12} A challenge has been identification of a sensitive and

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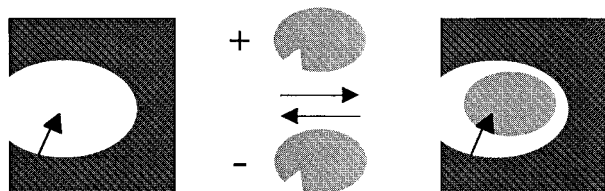
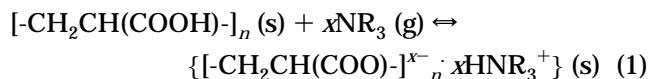


Figure 1. A schematic representation of the imprinted polymer film binding and releasing the target molecule.

convenient transduction mechanism, since many polymers do not afford an easily detectable and unambiguous change in properties upon analyte binding.^{10,13} Optical detection is an attractive methodology, allowing for nondestructive remote monitoring of analytes. Coupling the analyte-dependent emissive properties of CdSe to the selectivity of MIP films presents a versatile and straightforward methodology for constructing optical chemical sensors with the capability of customizing the selectivity for the target analyte.

A common strategy for creating such MIPs involves binding a target molecule to a monomer, polymerizing to create cross-links, and then removing the target molecule. In this work, rather than using a cross-linking methodology, we employ an alternate imprinting strategy that is similar to the phase inversion precipitation method established by Kobayashi et al.^{10,14} The carboxylic acid functionality of poly(acrylic acid) (PAA) films provides a natural binding mechanism for bases such as ammonia and alkylamines, eq 1 ($R = H, CH_3$), and also has a relatively high glass transition temperature of 379 K.¹⁵



Reversible reactions between gaseous amines and solid carboxylic acids have been shown in prior work. For example, gaseous ammonia and alkylamines have been intercalated into crystalline carboxylic acids through acid–base chemistry.^{16–18} More recently, proton transfer from poly(muconic acid) crystals to intercalated benzyl- and dodecylamines has been shown to be completely reversible.¹⁹

In previous studies, we have shown that PAA has a strong affinity for the CdSe surface.²⁰ Adsorption of the polymer from methanol solution leads to reversible quenching of PL intensity. Use of model compounds suggested that surface binding of PAA to CdSe involves the carboxylic acid proton.

In this paper we demonstrate that composite structures comprising an amine-imprinted PAA film atop an

emissive CdSe substrate can be used for selective chemical sensing. The acid–base chemistry underlying the film's reactivity is monitored through IR spectral changes, and the presence of amine analytes is detected through CdSe PL changes mediated by the imprinted PAA film. We present evidence from PL data that the polymer film acts as a sieve to control access to the CdSe surface based on the size of the imprinting amine. Chemical sensing implications of these results are also discussed.

Experimental Section

Materials. Single-crystal *c*-plates of n-CdSe with resistivity of $2 \Omega\text{-cm}$ ($\sim 5 \times 10^{15} \text{ cm}^{-3}$ carrier concentration) were purchased from Cleveland Crystals, Inc. The crystals were cut to a size of $\sim 5 \times 5 \times (1\text{--}3) \text{ mm}$. The Cd-rich (0001) face of the crystal was prepared by polishing the surface with $0.5 \mu\text{m}$ alumina and etching with a solution of bromine/methanol (1:15; v/v). The crystals were rinsed with methanol, sonicated for $\sim 20 \text{ min}$, and then dried with nitrogen gas prior to film deposition. Acrylic acid (AA) was obtained from Aldrich (99%), purified by fractional vacuum distillation, and used immediately, with all handling of the compound done under dry nitrogen. PAA ($M_w = 2000 \text{ g/mol}$; $M_w/M_n = 1.2$), AIBN (98%), anhydrous ammonia (99.99%), anhydrous methylamine (98+%), anhydrous dimethylamine (99+%), and anhydrous trimethylamine (99%) were purchased from Aldrich Chemical Co. and used as received. PAA samples of larger molecular weight (4 500, 20 000, 50 000, and 98 000 g/mol) were provided by Rohm & Haas and purified from aqueous solution by cation exchange along a column (AG 50W-X8 H-form, BioRad). The sodium salt of PAA ($M_w = 2100 \text{ g/mol}$) was obtained from Aldrich and used as received. Methanol (EM Science, 99.8%) was refluxed over magnesium methoxide, distilled prior to use, and handled under nitrogen that had been dried with CaSO_4 . All solutions were purged with and stored under nitrogen.

Imprinting. Imprinting was conducted both by polymerizing the AA monomer and by use of the polymer, PAA. To prepare the imprinted polymer film from the monomer, either ammonia or trimethylamine was bubbled through a $\sim 2 \text{ M}$ methanol solution of AA. The photoinitiator, AIBN (0.2 g/mL), was added to the monomer solution. The monomer was photopolymerized using 340 nm irradiation from a Model SP200 Bausch and Lomb mercury light source under a $\sim 200 \text{ mL/min}$ flow of gaseous ammonia or trimethylamine. Once the AA was polymerized, 3–4 drops of the solution were deposited onto the CdSe sample and dried under the amine flow. The amine was removed by vacuum ($\leq 30 \text{ mTorr}$).

To imprint from the polymer directly, methanol solutions of PAA ($M_w = 2000 \text{ g/mol}$) were prepared in concentrations of $50 \mu\text{M}$ in methanol. Ammonia or trimethylamine was then bubbled through the solution for at least 30 min . Two to four drops of the polymer solution were then deposited onto the CdSe substrate and dried under a flow of the amine. The amine was subsequently removed by exposure to vacuum ($\leq 30 \text{ mTorr}$) for 45 min . The coated CdSe sample was then mounted on a glass rod and secured by Teflon spacers for PL experiments. The film thickness was calculated to be $\sim 3000 \text{ \AA}$ based on a density of 1.22 g/cm^3 , assuming uniform thickness.¹⁵

Attempts were made to imprint films of the sodium salt of PAA using the methods described above. Because of the low solubility of the sodium salt of PAA in methanol, 1:1 (v/v) solutions of methanol and water were used.

Ellipsometry. Multiwavelength ellipsometry was conducted with an angle of 67.5° and wavelengths within a range of 343 to 1047 nm on a Verity Instruments Inc. Model TS10 ellipsometer. The film thickness obtained was consistent with that calculated above.

PL Studies. PL from the CdSe crystal was obtained by exciting the bare or coated CdSe sample with 458 or 488 nm light from a Coherent Radiation Model I90C argon ion laser; 594 nm light from a Melles-Griot Model 05-LHR-173 HeNe

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laser; or 633 nm light from a Melles-Griot Model 05-LHR-991 HeNe laser. In all cases an intensity of $<30 \text{ mW/cm}^2$ was used. Because the PL spectral distribution was insensitive to adsorbates at the low-resolution conditions employed ($\sim 1 \text{ nm}$), PL intensity was monitored at the band maximum of $\sim 720 \text{ nm}$. The PL response was collected at 8 s time intervals via a fiber optic interfaced to a 512-element Oriel Instaspec II diode array detector or an Oriel Instaspec II CCD detector.

Chemical sensing experiments were either conducted by using dry nitrogen as a reference ambient or by using vacuum ($<10 \text{ mTorr}$) as the reference. PL enhancements were measured relative to the baseline established by the reference. With a nitrogen reference ambient, gas was flowed through the cell at atmospheric pressure at a rate of 200 mL/min . The analyte gas was mixed with dry nitrogen, while maintaining a total flow rate of 200 mL/min .

IR Studies. All IR spectra were taken on a Mattson Polaris Model 53-10000 FTIR spectrometer. Samples were prepared by depositing 4 drops of $250 \mu\text{M}$ PAA ($M_w = 2000 \text{ g/mol}$) methanol solutions on a freshly polished and etched crystal of CdSe. The crystals were exposed to a static environment containing various partial pressures of ammonia or trimethylamine, which was combined with nitrogen to yield a total pressure of 1 atm.

The film absorbance was calculated by integrating the area of the peaks at 1550 and 1710 cm^{-1} , which correspond to the carbonyl stretches of the polymer's carboxylate anions and carboxylic acids, respectively.^{21–23} As previously described, an equilibrium constant for the binding of amine to the bulk imprinted PAA film, eq 1, can be estimated by using these integrated absorbance intensities and the relationship in eq 2,

$$K = [A_{\text{AM}}/A_{\text{PAA}}][\epsilon_{\text{PAA}}/\epsilon_{\text{AM}}][1/P_g] \quad (2)$$

where A_{AM} and A_{PAA} are the integrated absorption intensities of amine-bound film and the uncomplexed film, respectively; extinction coefficients for these species are represented by ϵ_{AM} and ϵ_{PAA} ; and partial pressure of amine is represented by P_g .⁷

Amine Mixtures. The response of ammonia-imprinted PAA films to mixtures of ammonia and trimethylamine was examined using IR and PL measurements. For the IR experiments, ammonia was bubbled through a $250 \mu\text{M}$ PAA ($M_w = 2000 \text{ g/mol}$) methanol solution for about 15 min. Four drops of the solution were deposited onto a freshly polished and etched crystal of CdSe, and solvent was removed under a flow of ammonia. The ammonia was removed from the PAA film by exposing it to vacuum ($<30 \text{ mTorr}$) for at least 60 min. The film was then exposed in turn to 0.10 atm of ammonia, 0.10 atm of trimethylamine, and to a mixture of 0.10 atm each of ammonia and trimethylamine for 2 min. Immediately after each exposure to amine, the IR spectrum was obtained. The absorption intensities at 1550 and 1710 cm^{-1} were then integrated. The amine was removed by exposure to vacuum again for about 60 min. PL experiments were conducted by using the same film preparation technique as for the IR experiments, except a solution of $50 \mu\text{M}$ PAA ($M_w = 2000 \text{ g/mol}$) methanol solution was used. The semiconductor film was exposed to the same collection of gases, and PL changes were determined relative to the baseline.

Co-Imprinting. To co-imprint the polymer, ammonia and trimethylamine were bubbled simultaneously through a $50 \mu\text{M}$ methanol solution of PAA ($M_w = 2000 \text{ g/mol}$) at equal partial pressures totaling 1 atm for about 30 min; the flow rate for each gas was 10 mL/min . Two to four drops of the polymer solution were then deposited onto the CdSe substrate and dried under a flow of the amines. The amines were subsequently removed by exposure to a vacuum ($\leq 30 \text{ mTorr}$) for 45

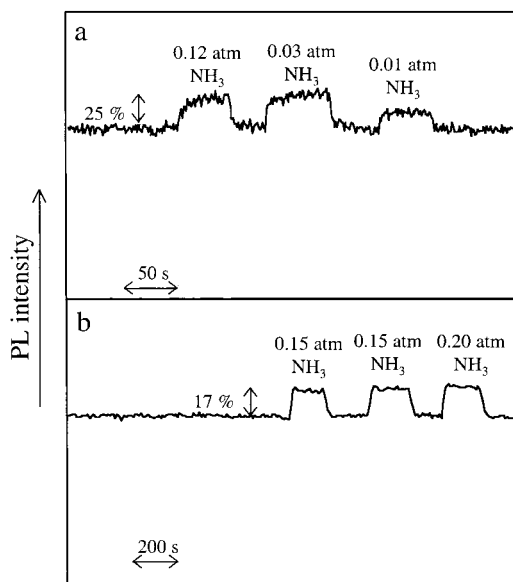


Figure 2. Changes in PL intensity resulting from exposure to the indicated pressures of ammonia for (a) an etched CdSe crystal and (b) a CdSe crystal coated with an ammonia-imprinted PAA (AI-PAA) film. In both sets of experiments the PL was excited at 633 nm and monitored at 720 nm.

min. The coated CdSe sample was then mounted on a glass rod and secured by Teflon spacers for PL experiments.

Results and Discussion

Upon ultra-band gap excitation ($E_g \sim 1.7 \text{ eV}$; $\lambda_{\text{max}} \sim 720 \text{ nm}$), n-CdSe samples exhibit red band-edge PL. The PL was monitored in gas-phase adsorption studies of amines that were conducted with four different types of CdSe surfaces: (1) etched only; (2) PAA-coated; (3) ammonia-imprinted (AI-PAA); and (4) trimethylamine-imprinted (TI-PAA). In the latter two cases, imprinting involved saturating a methanolic PAA solution ($M_w = 2000 \text{ g/mol}$) with the ammonia or trimethylamine, depositing drops of the solution onto the substrate, and, after drying in the presence of amine, removing the ammonia or trimethylamine under vacuum and leaving behind receptor sites in the PAA matrix. We also attempted to investigate films of the sodium salt of PAA, with and without ammonia present (prepared from methanol/water (1:1 v/v) solutions because of poor solubility of the salt in methanol). Because the PL results were found to be irreproducible, no further studies were conducted with these films.

Adsorption of ammonia onto the etched-only surface and imprinted PAA-coated surfaces causes an enhancement in PL intensity, consistent with the Lewis basicity of ammonia. For example, a typical response is shown in Figure 2a for adsorption of ammonia onto the etched-only surface. This response is typical for the bare surface of CdSe; for the samples studied PL enhancements to 0.10 atm ammonia ranged from 10 to 30%. In general, when the shiny Cd-rich (0001) etched surface of CdSe is exposed to gaseous ammonia and its methyl derivatives, reversible PL enhancements are observed relative to a nitrogen or vacuum reference ambient.^{3,24} In comparison, AI-PAA-coated CdSe responds to ammonia

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but not to trimethylamine. Like the bare surface, both ammonia and trimethylamine elicit PL responses from TI-PAA film-coated CdSe containing larger receptor sites. In contrast, an unimprinted PAA-coated CdSe surface does not respond to ammonia or trimethylamine, demonstrating that imprinting is required for analyte access to the CdSe surface.

The magnitude of the PL response can be quantified by the dead-layer model, which describes the effect of the analyte on the electronic structure of the semiconductor.¹ The change in PL intensity is described in terms of analyte-induced changes in the thickness of a non-emissive region near the surface of the semiconductor, called a "dead layer". The quantitative form of the dead-layer model is

$$PL_{\text{ref}}/PL_x = \exp(-\alpha'DD) \quad (3)$$

Here, PL_{ref} represents the PL intensity in the nitrogen reference ambient; PL_x represents the PL intensity in the presence of the analyte; $\alpha' = (\alpha + \beta)$ is the sum of the absorptivities for the exciting and emitted light; and $\Delta D = (D_{\text{ref}} - D_x)$ is the reduction in the dead-layer thickness caused by adsorption. This simple form of the dead-layer model assumes that the surface recombination velocity (S) is unaffected by adsorption or very large in both ambients ($S \gg L/\tau$ and $S \gg \alpha L^2/\tau$, where L and τ are the minority carrier (hole) diffusion length and lifetime, respectively). The model can be tested by excitation at several different wavelengths to determine whether a constant value of ΔD is observed. For the bare CdSe surface, typical maximum values determined for the reduction in dead-layer thickness have been reported to be ~ 100 Å for adsorption of ammonia.²⁴

The magnitude of the PL response generally increases with analyte concentration, as shown in Figures 2a and 3a for ammonia adsorption onto the etched-only surface. This concentration dependence permits an estimate of the adsorbate binding constant using the Langmuir adsorption isotherm model.²⁵ The model is quantitatively represented by eq 4, where K is the equilibrium constant for adsorption, and P is the analyte partial pressure.

$$1/\theta = 1 + 1/(KP) \quad (4)$$

The fractional surface coverage, θ , is estimated from the fractional changes in dead-layer thickness: When the PL changes have saturated, PL_{sat} , θ is taken to be 1; the PL intensity in the reference ambient, PL_{ref} , corresponds to $\theta = 0$; at intermediate coverages, the PL intensity is designated as PL_x and defined by eq 5.

$$\theta = \{\ln[PL_{\text{ref}}/PL_x]\}/\{\ln[PL_{\text{ref}}/PL_{\text{sat}}]\} \quad (5)$$

For ammonia adsorption onto the etched-only surface (Figure 3a), such an analysis yields a binding constant of $750 \pm 250 \text{ M}^{-1}$ ($30 \pm 10 \text{ atm}^{-1}$).

In the sections below we characterize the interactions of the PAA/CdSe composite structures with ammonia and trimethylamine by PL and IR measurements and discuss implications for chemical sensing. We contrast

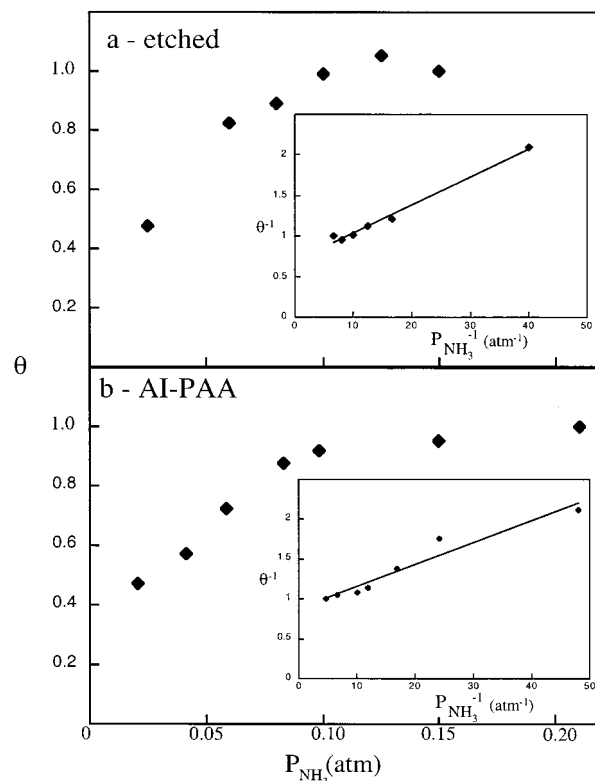


Figure 3. Fractional surface coverage, θ , determined using eq 5, as a function of ammonia pressure for (a) an etched CdSe crystal and (b) a CdSe crystal coated with an ammonia-imprinted PAA (AI-PAA) film. The insets show the same data as double reciprocal plots, yielding equilibrium constants for (a) and (b) of $750 \pm 250 \text{ M}^{-1}$ ($30 \pm 10 \text{ atm}^{-1}$) and $1000 \pm 500 \text{ M}^{-1}$ ($40 \pm 20 \text{ atm}^{-1}$), respectively. In both sets of experiments the PL was excited at 633 nm and monitored at 720 nm.

these results with those for the PAA-coated and etched-only CdSe surfaces.

PAA-Coated CdSe and IR Studies. Examination of the nonimprinted films on CdSe provides evidence that imprinting is critical for providing amines with access to the PAA-coated CdSe surface. When CdSe is coated with a film of PAA deposited from nitrogen-saturated methanolic solutions of the polymer by evaporation of solvent, the PL response to ammonia or trimethylamine is lost (no change in PL intensity or less than 5% change in PL intensity). This result suggests that the analyte molecules are physically unable to reach and interact with the semiconductor surface. As expected, when the PAA was removed by redissolving the polymer film in methanol, the uncoated CdSe surface once again responded to amines. Unlike the PAA-coated film, imprinted-PAA films provide target molecules access to the CdSe surface.

Even though the PAA coating eliminated the CdSe substrate's PL response to ammonia and trimethylamine, we could demonstrate using IR spectroscopy that the film is nonetheless reacting with these analytes according to eq 1. Figure 4a presents the IR spectrum of the PAA film as deposited onto a CdSe substrate. The peak at 1710 cm^{-1} is characteristic of the carbonyl stretching frequency of a carboxylic acid.^{21–23} Upon exposure of this film to ammonia or trimethylamine gas, a new peak appears at 1550 cm^{-1} , Figure 4b, indicative of the formation of carboxylate anion.²¹ Similar spectral shifts are observed in solution IR experiments when a

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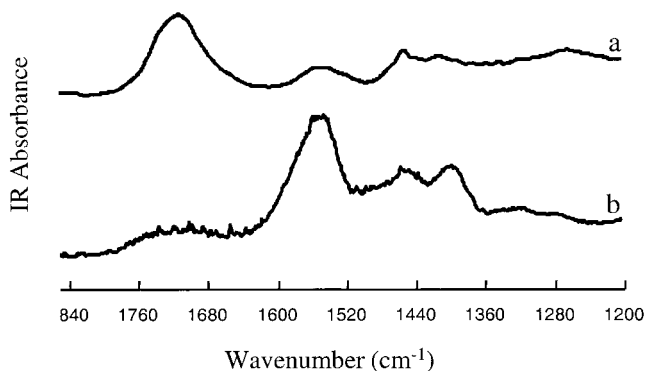


Figure 4. IR absorption spectra for a PAA film deposited onto CdSe in the presence of (a) nitrogen and (b) ammonia, both at 1 atm.

methanolic PAA solution is saturated with ammonia or trimethylamine.

Ammonia- and Trimethylamine-Imprinted PAA CdSe Studies. *Preparation of Imprinted Coatings.* Our initial imprinting studies were conducted by purging a methanolic solution of acrylic acid (AA) monomer with anhydrous amine and then polymerizing to form PAA films from which the amine could subsequently be removed under vacuum. As coatings on CdSe substrates, these films yielded indistinguishable IR and PL results in subsequent binding experiments from those formed directly from amine-purged PAA methanolic solutions. We thus used the latter, simpler procedure for routine preparation of imprinted PAA films. It is also noteworthy that repetition of the experiments described in this study using PAA films of higher molecular weights (4 500, 20 000, 50 000, and 98 000 g/mol) yielded similar results to those obtained with 2 000 g/mol molecular weights.

Ammonia-Imprinted PAA Coatings. PAA films on CdSe that had been imprinted with ammonia (AI-PAA) were exposed to vacuum to remove most of the ammonia prior to conducting PL experiments. It is important to note that the ammonia-induced IR changes are not completely reversible; about 5% of the ammonia molecules appear to be irreversibly bound to the bulk AI-PAA film. The PL responses are, however, reversible, indicating that the adsorption of ammonia onto or near the semiconductor surface is reversible.

The interaction of ammonia with the binding sites in the AI-PAA films was studied by IR spectroscopy. For ammonia, the onset of IR spectral changes for the film occurs at ~ 0.002 atm, and saturation is evident by ~ 0.1 atm. Using fractional integrated IR absorption changes as a measure of θ leads to an equilibrium constant for film binding, eqs 1 and 2, of $\sim 10^3 \text{ M}^{-1}$ ($\sim 10^1 - 10^2 \text{ atm}^{-1}$) for a variety of film samples. Comparison of IR and PL binding constants, described below, for ammonia on AI-PAA films suggests that the distribution coefficient for binding of these analytes is on the order of unity, i.e., there appears to be no significant preference for binding of the analyte in the bulk film relative to the semiconductor-film interface.⁷

When AI-PAA-coated CdSe samples were exposed to ammonia, reversible PL enhancements of as much as $\sim 20\%$ relative to the nitrogen reference ambient baseline were observed. Representative data are shown in Figure 2b. The response to ammonia is similar to that

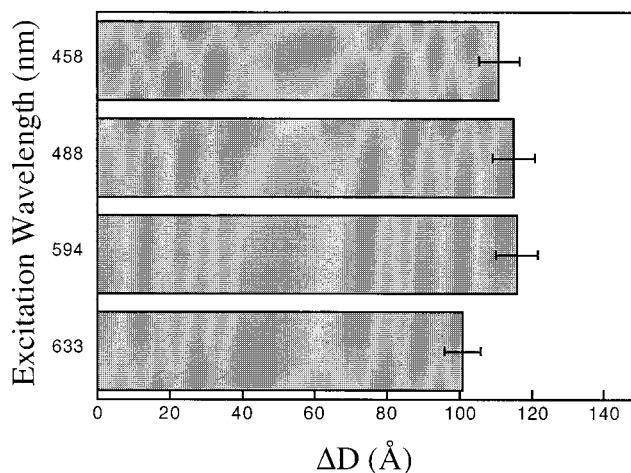


Figure 5. Maximum ΔD values calculated from PL enhancement data using eq 3, for a film of ammonia-imprinted PAA (AI-PAA) upon exposure to ≥ 0.2 atm ammonia; values correspond to maximum contraction of the dead-layer thickness. The horizontal lines associated with each bar represent the error associated with the ΔD value. All data were collected from the same surface and film.

of the bare, etched surface in percent enhancement and rate of response. For the various AI-PAA films, the responses to 0.10 atm ammonia range from about 10% to 30% enhancements in the PL intensity. The maximum PL enhancements yielded good fits to the dead-layer model, as shown in Figure 5. A maximum reduction in dead-layer thickness of $\sim 100 \text{ Å}$ is shown by these data. This value is similar to that found for ammonia adsorption onto the bare CdSe surface, indicating that the presence of the film coating has little effect on ammonia-CdSe surface interactions. In contrast, exposure of the same AI-PAA-coated CdSe sample to the more sterically demanding trimethylamine yielded no PL response, suggesting that the accessibility of this molecule is physically restricted relative to ammonia. This physical picture is supported by the observation that the IR spectrum of an AI-PAA film exposed to trimethylamine resulted in a change in the integrated absorption intensity that was about one-third of that found for the same pressure of ammonia. For comparison, methylamine and dimethylamine were also briefly examined, enabling us to determine the trend in PL response as being $\text{NH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} = (\text{CH}_3)_3\text{N} \sim 0$. This trend is notably different from that reported for the bare CdSe surface (vide supra) and attests to the film's ability to impart binding selectivity.³

The adsorption binding profiles of ammonia on AI-PAA-coated CdSe fell into two classes, each about equally likely to be observed under our preparative conditions. One class of AI-PAA films led to CdSe PL data that were virtually indistinguishable from those of the bare CdSe surface, suggesting that comparable adsorbate-semiconductor interactions are present in both cases, despite the presence of the imprinted film. Ammonia responses with such an AI-PAA film are shown in Figure 3b. For this sample, an interfacial binding constant of $1000 \pm 500 \text{ M}^{-1}$ ($\sim 40 \pm 20 \text{ atm}^{-1}$) was determined. Values were typically in the range of $\sim 10^3 \text{ M}^{-1}$ ($\sim 10^1$ to 10^2 atm^{-1}) for the set of seven samples examined. This similarity, along with the comparable ΔD values, provides further evidence that the

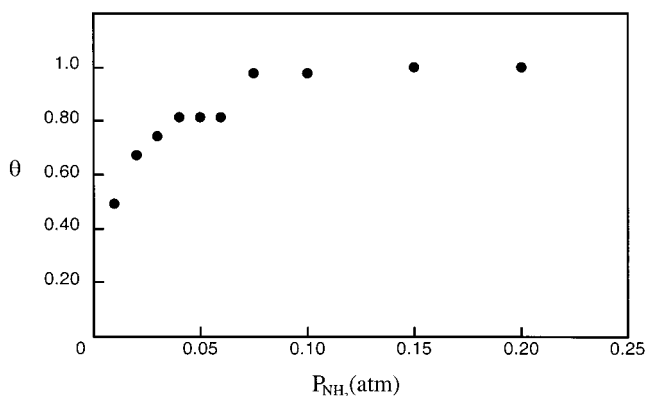


Figure 6. Fractional surface coverage, θ , determined using eq 5, as a function of ammonia pressure for a CdSe crystal coated with an ammonia-imprinted PAA (AI-PAA) film. A kink that appears at ~ 0.05 atm separates low and high-pressure regimes. The PL intensity at this point, corresponding to $\theta \sim 0.8$, was used as the saturation pressure for the low-pressure portion of this plot, and as the baseline for the high-pressure portion of the plot. Application of the Langmuir model (eq 4) to each portion separately yields binding constants of $2000 \pm 300 \text{ M}^{-1}$ ($80 \pm 12 \text{ atm}^{-1}$) and $1000 \pm 400 \text{ M}^{-1}$ ($40 \pm 16 \text{ atm}^{-1}$) for the low-pressure and high-pressure regimes, respectively.

imprinted film acts as a sieve; the AI-PAA film allows only the ammonia molecules to adsorb onto the CdSe surface and does not appear to interfere with the ammonia-surface interaction.

About half of the AI-PAA-coated samples yielded isotherms that had a kink, comprising the second class of PL binding profiles (Figure 6). Typically, the kink occurred at pressures of between 0.02 and 0.08 atm and at $\sim 80\%$ of the maximum PL enhancements, which occurred at saturation pressures of ~ 0.1 atm. The kink may be the result of at least two different kinds of binding sites. Application of the Langmuir model separately to each section of the concentration profile shown in Figure 6 yielded a binding constant of $\sim 2000 \pm 300 \text{ M}^{-1}$ ($\sim 80 \pm 12 \text{ atm}^{-1}$) for data in the low-pressure regime and $\sim 1000 \pm 400 \text{ M}^{-1}$ ($\sim 40 \pm 16 \text{ atm}^{-1}$) for the high-pressure regime. We were unable to identify differences in preparative conditions leading to the two classes of concentration profiles.

Many multistep isotherms such as the kinked isotherm of Figure 6 have been seen for a variety of adsorption processes and have been ascribed to multilayer adsorption.^{26–30} Further investigations of the imprinted films may clarify the cause of these kinks; however, a plausible explanation of the effect is the presence of two types of binding sites. It is possible that some of the binding sites at or near the surface of the CdSe are more difficult for the target molecule to reach. The first binding sites filled are the more kinetically favored sites, and only at higher concentrations do the target molecules bind to the less favored binding sites.

Trimethylamine-Imprinted PAA Coatings. Trimethylamine-imprinted PAA films (TI-PAA) were prepared for CdSe with the same methods used for AI-PAA films. For reaction of trimethylamine with TI-PAA films, the IR changes were small, typically 10% or less, and erratic, thereby preventing us from estimating a binding constant. Upon exposure to ammonia, these same films showed much greater reactivity, corresponding to binding constants such as those calculated from PL changes seen for ammonia on AI-PAA films, $\sim 10^3 \text{ M}^{-1}$ ($\sim 10^1$ – 10^2 atm^{-1}).

In contrast to the AI-PAA films that prevented trimethylamine from eliciting a PL response, TI-PAA films initially yielded reversible PL enhancements with ammonia and all three alkylamine analytes examined. The PL responses to 0.10 atm trimethylamine for these films range from 5 to 15% enhancements for the various films tested. This response presumably reflects a more sterically accessible film, resulting from the larger size of trimethylamine. However, repeated exposure led to irreversible responses to trimethylamine. In contrast, reversible PL responses to ammonia were observed over 10 cycles. The adsorption isotherm for ammonia on a TI-PAA film is similar to the nonkinked adsorption isotherm on AI-PAA shown in Figure 3b.

Sensor Considerations

In addition to analyte selectivity, other considerations for employing the composite emissive sensors reported herein include speed of response and robustness. As Figures 2a and 2b illustrate, the presence of these films at the thicknesses we have employed ($\sim 3000 \text{ \AA}$) does not significantly lengthen the time needed to observe a PL response. For both adsorption and desorption, PL responses typically require on the order of 30 s without a film and about a minute with a film. Films of AI-PAA still retain their ability to respond to ammonia and not to trimethylamine after extended exposure to oxygen. Overnight exposure to humid air causes the AI-PAA-coated CdSe to begin to show small PL responses to trimethylamine ($<5\%$) while still retaining the response to ammonia. All of the experiments described above were conducted at room temperature, below the glass transition temperature of PAA, 379 K.¹⁵ After heating an AI-PAA-coated CdSe sample above the glass transition temperature, the PL baseline response was no longer stable, suggesting that the film and/or semiconductor surface had been compromised.

The films that we have prepared lend themselves to studies of gaseous mixtures, as commonly found in many sensor applications. As an example, we have examined mixtures of ammonia and trimethylamine. When an ammonia-imprinted PAA film was exposed to a mixture containing 0.10 atm each of ammonia and trimethylamine, the changes in IR absorption for the carboxylate peak at 1550 cm^{-1} were smaller for the combination of gases than when only 0.10 atm of ammonia was present. In the corresponding PL experiment the enhancement for the mixture of ammonia and trimethylamine (each at 0.10 atm) was diminished relative to the enhancement seen with 0.10 atm of ammonia alone. We presume that the steric bulk of trimethylamine may block receptor sites and prevent ammonia molecules from binding to the film at or near the CdSe surface.

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We have also conducted preliminary experiments with PAA films co-imprinted using equal flow rates of ammonia and trimethylamine. As might be expected, both ammonia and trimethylamine elicited PL responses. Such film structures might be used to detect combinations of gases in mixtures. Experiments to further characterize these and related systems are in progress in our laboratories.

Conclusion

Our experiments demonstrate that, in contrast to a bare CdSe surface, which cannot discriminate in its PL response between ammonia and trimethylamine, coating the semiconductor surface with an ammonia-imprinted poly(acrylic acid) film imparts selectivity: a PL response is seen with ammonia but not with trimethylamine. Trimethylamine-imprinted poly(acrylic acid) films do not provide this selectivity, presumably

reflecting a more sterically accessible coating. These substantial film differences will be investigated in future experiments with techniques such as atomic force microscopy, which should enable us to better characterize the role of film morphology in these composite systems.

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