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Reversible Photoluminescence Quenching of CdSe/ZnS Quantum Dots Embedded in Porous Glass by Ammonia Vapor

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Abstract

The photoluminescence response of semiconductor CdSe/ZnS quantum dots embedded in a borosilicate porous glass matrix to exposure to ammonia vapor is investigated. Formation of surface complexes on the quantum dots results in quenching of the photoluminescence and a shortening of the luminescence decay time. The process is reversible, desorption of ammonia molecules from the quantum dot surface causes the photoluminescence to recover. The sensitivity of the quantum dot luminescence intensity and decay time to the interaction time and the reversibility of the photoluminescence changes makes the CdSe/ZnS quantum dot in porous glass system a candidate for use as an optical sensor of ammonia.

Keywords: Quantum dots, ammonia, porous glass, photoluminescence

1. Introduction

Ammonia vapor is a noxious, toxic gas, causing irritation of mucous membranes, toxic pulmonary edema, damage to the nervous system and, in high concentrations, death [1]. Fortunately, ammonia has a pungent odor, allowing detection of high concentrations by the human nose.

There are many situations where it is necessary to detect ammonia at ultra-low concentrations, such as in the fields of environmental monitoring, the automotive and chemical industry and also in medical diagnostics [2]. For example, detection of ammonia in human breath is a marker for several diseases [3, 4]. Optical techniques offer considerable promise for sensing ammonia [5, 6].

In this study, we propose using changes in the luminescence signal from quantum dots embedded in a borosilicate porous glass caused by ammonia vapor exposure in order to sense the vapor.

Semiconductor quantum dots (QD) are nanocrystals in which quantum size confinement effects are observed. The energy structure and optical properties of QDs depend on their size. QDs have extended absorption bands with large optical extinction coefficients. They typically emit intense photoluminescence signals and are photostable [7]. Chemical interaction of QDs with certain compounds can result in changes in their optical properties. In particular, interaction of semiconductor CdSe/ZnS quantum dots with vapors containing nitrogen results in luminescence quenching [8], with the amount of luminescence quenching correlated with the concentration of the vapor.

The primary function of the porous glass is to concentrate the analyte vapors via the highly developed, inner pore surface, decreasing the detection threshold [9, 10]. Combining QDs with the porous glass allows the design of a new class of optical sensors with enhanced photostability and high sensitivity.

In this study, we investigate the photoluminescence properties of CdSe/ZnS QDs in borosilicate porous glass when exposed to ammonia vapor. It is found that the interaction with ammonia vapor leads to a quenching of the QD luminescence, together with a reduction in the luminescence decay time. Desorption of the ammonia molecules from the porous glass matrix leads to a recovery of the luminescence signal from the QDs to its initial level. This data clearly shows that CdSe/ZnS quantum dots embedded in porous glasses have considerable potential for application as a sensing element for vapors containing nitrogen.

2. Experimental.

Semiconductor CdSe/ZnS QDs were synthesized using the method described in [11]. The QDs have the following characteristics: an average QD core size of 2.5 nm, an exciton absorption band at $\lambda = 510$ nm, a luminescence peak at $\lambda = 530$ nm, a Full Width at Half Maximum (FWHM) in the luminescence band of 35 nm, a molar extinction coefficient $\varepsilon_{510} = 4.7 \cdot 10^4 \text{ mol}^{-1} \cdot \text{L QD cm}^{-1}$, and a PL quantum yield (Q) in chloroform solution of 13 %.

NPG-17 porous borosilicate glass [12] is used as a matrix to contain the CdSe/ZnS QDs. The porous glass has the following characteristics: an average pore diameter of 17 nm, a free sample volume, $\sigma = 55\%$ and a specific porous surface of between 100-120 m^2/g . In these experiments, $10 \times 10 \text{ mm}^2$ samples of 1 mm thickness were used.

CdSe/ZnS quantum dots were incorporated into the porous glass via five minute stepwise immersion of the sample into the QD chloroform solution, with a QD concentration of about 10^{-6} mol/L . The total immersion time was 45 minutes. Every 5 minutes, the sample was withdrawn from the solution in order to measure the absorption and photoluminescence

(PL) spectra and the PL decay time. Before the measurements, the sample surfaces were thoroughly washed with chloroform to remove QDs from the surface. Next, the samples were dried at room temperature for several minutes until they became completely transparent, indicating that chloroform has been removed from the pores.

The average surface density of the QDs adsorbed on the inner pore surface of the samples (ρ) can be estimated from a modified Beer's law:

$$\rho = \frac{D}{\varepsilon \cdot l} \cdot \frac{V}{S} \quad (1),$$

where D is the optical density of the sample at the QD exciton absorption band, ε is the molar extinction coefficient at the maximum of the QD excitonic band; V and l are the measured volume and thickness of the porous glass sample, respectively, $S = m \cdot \sigma$ is the total square of the inner pore surface of the sample, where m is the weight of the sample.

If we assume that quantum dots are uniformly distributed on the inner surface of the pore, the average distance between the QD surfaces (R) can be estimated as follows:

$$R = \frac{1}{\sqrt{\pi \cdot \rho \cdot N_A}} - 2r_{QD} \quad (2),$$

where N_A is the Avogadro constant; r_{QD} is the QD average radius.

The interaction of ammonia vapor with the QDs embedded in the porous glass was investigated as follows. The sample was quickly placed in a hermetically sealed 16 ml box after 5 μ l of 10% aqueous ammonia solution was dropped onto the bottom of the box. Under these conditions, the ammonia vapor pressure is lower than the saturation vapor pressure, so the ammonia evaporates completely. The ammonia vapor concentration during the experiment was estimated to be about 1.7 $\times 10^{-3}$ mol/L. The sample did not contact the ammonia solution, so the QDs only interact with the ammonia vapor penetrating the pores. Samples were exposed stepwise to ammonia vapor for a total of 20 minutes at 5 minute intervals. Every 5 minutes, the sample was withdrawn from the box for reference PL spectra and decay time measurements. The ammonia exposure duration was limited to 20 minutes in total, since our preliminary experiments showed that the PL response of the samples was stable one hour after withdrawal.

A Fluorat-02-Panorama spectrofluorometer (Lumex inc., Russia) and a UV-Probe 3600 spectrophotometer (Shimadzu, Japan), were used for registration of the steady-state photoluminescence and absorption spectra of the samples, respectively. In order to measure the PL spectra, the samples were placed in a standard sample compartment within the spectrofluorometer at a 45⁰ angle. Time-resolved luminescence measurements in back-scattering geometry were performed by a MicroTime 100 laser scanning luminescent

microscope (Pico Quant, Germany), with 100 ps time resolution. 405 nm radiation from a 5 MHz pulsed diode laser was used for PL excitation. Spectral selection of the PL from the samples was performed using a set of interference filters with a Full Width at Half Maximum of 10 nm in the wavelength range from 500 nm to 570 nm. The average decay time was calculated using the formula: $\langle \tau_{av} \rangle = \sum A_i \tau_i^2 / \sum A_i \tau_i$, where A_i and τ_i are the amplitude and decay time of the i -th component, respectively.

3. Results and discussion.

3.1. Optical properties of CdSe/ZnS QDs in porous glass matrices.

Absorption and PL spectra taken from the porous glass sample after immersion in a solution of CdSe/ZnS QDs in chloroform for various times are presented in Figure 1, together with the spectra from a colloidal solution of QDs. The dependence of the sample optical density on immersion time and the PL intensity as a function of the QD concentration in the porous glass are shown as insets in Figures 1a and 1b, respectively.

Figure 1a demonstrates that the optical density of the sample, or the QD concentration in the sample, $C = D/\varepsilon \cdot l$, increases linearly with immersion time for QD concentrations of up to $6.5 \cdot 10^{-5}$ mol/L. The PL intensity from the embedded QDs also increases linearly with QD concentration, up to a concentration of about $3 \cdot 10^{-5}$ mol/L (see insert in Figure 1b). At higher QD concentrations, the PL intensity from the QDs remains constant, due to absorption of the incident light. For this reason, we investigated the interaction of QDs in porous glass samples with ammonia vapor at QD concentrations of $2 \cdot 10^{-5}$ mol/L.

Analysis of the spectra showed that the spectral position and shape of the absorption and PL bands of the QDs in the glass is similar to those of QDs in chloroform solution over a range of QD concentrations. This indicates that the CdSe/ZnS quantum dots embedded in the porous glass matrices interact very weakly with each other. If this were not the case, Förster Resonance Energy Transfer (FRET) between neighboring QDs in close packed ensembles of the nanocrystals differing slightly in size will change the shape of the PL band. The PL peak is red shifted and, in addition, the PL decay time is lowered at the higher energy wing of the inhomogeneously broadened PL band when compared with the lower energy wing [13]. We compared the PL decay time from the QDs in both the porous glass and the chloroform solution at various detection wavelengths by using a set of narrow band interference filters. In both cases, the PL decay can be well fitted by a biexponential function. The average PL decay time, $\langle \tau \rangle$, as a function of detection wavelength is presented in Figure 2 for QDs in chloroform and in porous glass. The data for the QDs in

porous glass shows no evidence of interdot dipole-dipole interactions that are characteristic of FRET for close packed QDs. Simple estimates using formulae (1) and (2) show that the average surface density of the quantum dots adsorbed on the inner surface of the pores in our samples varies from $6.5 \cdot 10^{-15}$ mol/L·cm² to $1.7 \cdot 10^{-14}$ mol/L·cm². So, the average distance between the quantum dots is in the range 35 - 50 nm. This inter-dot distance is too great to allow efficient FRET between QDs of different sizes [14]. Clearly, our data indicates that the CdSe/ZnS quantum dots embedded in the porous glass matrices from a chloroform solution do not interact with each other.

We observed an almost 40% increase in the average PL decay time for QDs embedded in the porous glass (32 ± 2 ns) as compared with those in the chloroform (20 ± 2 ns). The reasons for this are, at present, unclear. It is possible that adsorption of quantum dots on the inner surface of the pores decreases the number of QD surface defects responsible for nonradiative deactivation of the QD excited state. Alternatively, it may be that the PL from the QDs in chloroform solution is slightly quenched by the presence of the chloroform molecules which are absent from the porous glass samples.

3.2. CdSe/ZnS QD interaction with ammonia vapor.

Exposure of the porous glass matrices with embedded CdSe/ZnS QDs to ammonia vapor results in significant quenching of the QD photoluminescence and a reduction in the average PL decay time. Typical dependencies of the PL intensity and average PL decay time versus ammonia exposure time are shown in Figure 3.

From Figure 3, a reduction in the PL intensity and a decrease in the average PL decay time with increasing ammonia exposure duration is apparent (curves 1 and 2, respectively). These results show that increasing the duration of ammonia exposure leads to an increase in the number of ammonia molecules on the QD surface and a consequent quenching of the QD luminescence and reduction in the QD PL decay time. We assume that ammonia molecules coordinate on the QD ZnS shell via surface Zn ions. Similar results have been observed for CdSe QDs complexing with pyridine molecules [15],

The mechanism leading to luminescence quenching of QDs and the reduction in PL decay time is unclear at present. Nonradiative resonant energy transfer or electron transfer are considered to be the principle mechanisms responsible for QD photoluminescence quenching via interaction with organic molecules [15, 16, 18-21]. In our case, however, nonradiative resonant energy transfer from QDs to the ammonia molecules cannot occur due to the absence of appropriate electronic transitions in the ammonia molecule in the spectral region of interest. Electron transfer is also improbable for a QD/ammonia pair due to the

absence of a π -electron system. Also, the low energy of the Highest energy Occupied Molecular Orbital (HOMO) of -10.5 eV [16] of ammonia makes electron transfer unlikely. QD PL quenching may originate from a long-range electronic-to-vibrational energy transfer [17] from the QD to the NH-vibration of the ammonia molecule. Another possible reason for nonradiative photoexcitation energy losses is the appearance of new local sites on the QD surface at the points of coordination of the ammonia molecules, which may act as photoelectron traps. This mechanism is considered in the literature [20]. Additional studies are now underway in order to examine this problem.

It has been found that storage of the ammonia-treated samples under ambient conditions for 7 days resulted in a recovery of the PL signal to ~35% of the initial, untreated, value accompanied by an increase of the average PL decay time from 20 ns to 22.5 ns. This indicates that desorption of ammonia molecules from the QD surface is occurring. This can be accelerated by vacuum degassing of the ammonia-treated samples. Indeed, a 10 min vacuum degassing of the sample at a pressure of ~1 torr led to a complete recovery of the PL intensity and decay time, demonstrating that complete desorption of the ammonia molecules from the QD surface has occurred. Photoluminescence spectra from samples of porous glass with QD/ammonia complexes after 7 days storage under ambient conditions and the spectrum following vacuum degassing for 10 min presented in Figure 4 are very similar to the spectrum from the un-treated sample shown in Figure 1.

The dependence of the PL properties of QDs on the number of ammonia molecules adsorbed on their surface suggests using CdSe/ZnS quantum dots embedded in the porous glass as sensor elements for the quantitative detection of ammonia vapor. Reusability of the sensor element is a key requirement for use in a practical sensor system. Therefore, we examined the ability of CdSe/ZnS QDs embedded in porous glass matrices to re-adsorb ammonia molecules following a complete cycle of adsorption/desorption of ammonia molecules. We found that the dependencies of QD PL quenching and the reduction in the QD PL decay time are identical to those exhibited by the sample during the initial adsorption/desorption cycle. We conclude that the CdSe/ZnS quantum dots embedded in porous glass matrices retain their photophysical properties after interaction with ammonia molecules and so this system could be used as reusable sensor for ammonia vapor detection.

4. Conclusion

In conclusion, immersion of borosilicate porous glass samples in a colloidal chloroform solution of semiconductor CdSe/ZnS quantum dots leads to adsorption of the nanocrystals on the inner surface of the glass pores. Exposure of the porous glass samples

with embedded CdSe/ZnS QDs to ammonia vapor results in effective quenching of the QD photoluminescence and a reduction in the average PL decay time due to formation of QD/ammonia complexes on the surface of the CdSe/ZnS QDs. Vacuum degassing of the sample causes complete removal of the ammonia molecules from the QD surface, restoring the PL intensity and decay time observed from the QDs. We propose that porous glass matrices with embedded CdSe/ZnS quantum dots could be used as a highly sensitive element for the quantitative vapor detection of nitrogen containing compounds.

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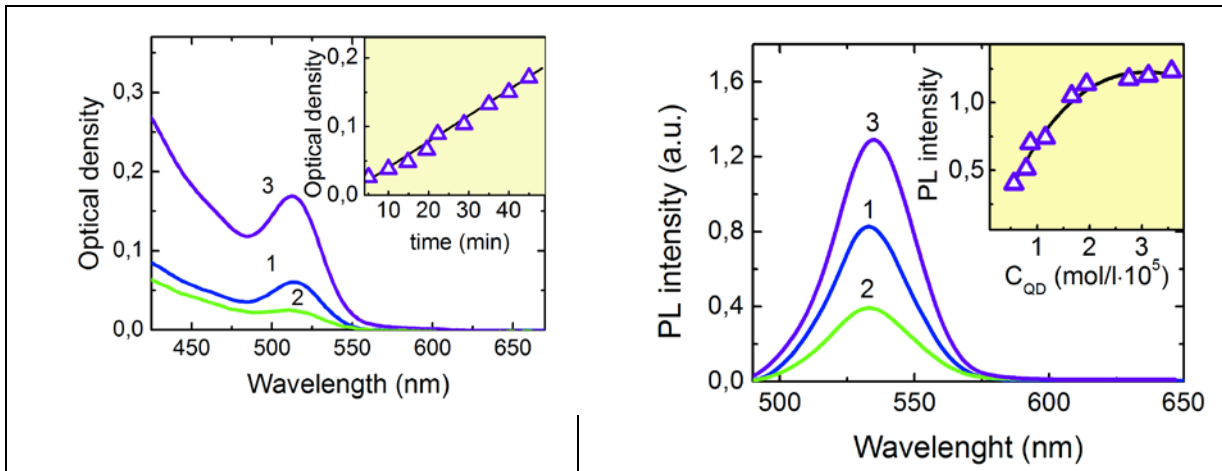


Fig. 1. Absorption (a) and photoluminescence (b) spectra of CdSe/ZnS QDs in chloroform solution (1) and embedded in porous glass for 5 min (2) and 45 min (3) immersion times. The PL was excited by 405 nm radiation. Insert in (a) shows the dependence of the sample optical density on immersion time while the insert in (b) represents the PL intensity as a function of QD concentration (C_{QD}) in the porous glass sample.

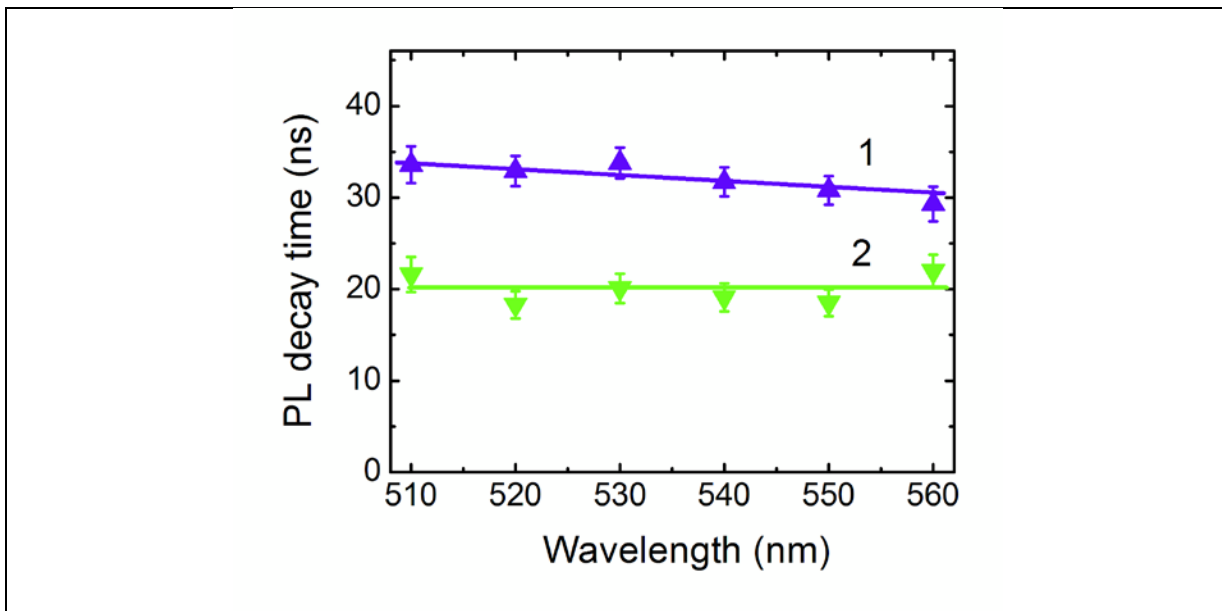


Fig. 2. CdSe/ZnS QD photoluminescence average decay time $\langle \tau \rangle$ as a function of detection wavelength for QDs in porous glass (1) and in chloroform solution (2). The PL was excited by a 405 nm pulsed diode laser.

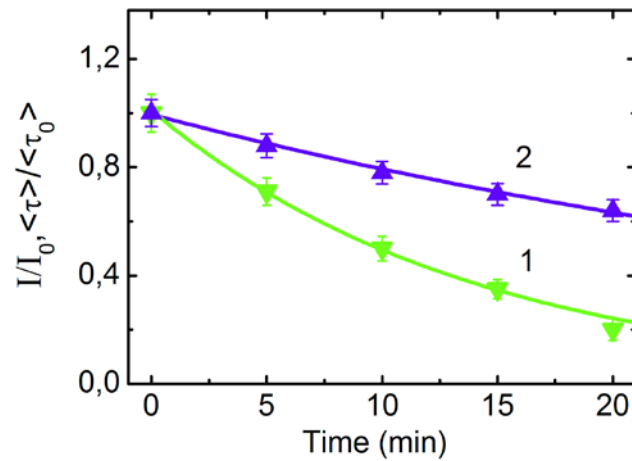


Fig.3. Typical dependencies of the QD PL intensity (1) and the average QD PL decay time (2) on exposure time for a sample of CdSe/ZnS QDs in porous glass exposed to ammonia vapor with a concentration C_a of about 1.7×10^{-3} mol/l. The PL was excited by 405 nm light. I/I_0 and $\langle \tau \rangle / \langle \tau_0 \rangle$ are the normalized QD PL intensity and average decay time, respectively. The curves are guides to the eye.

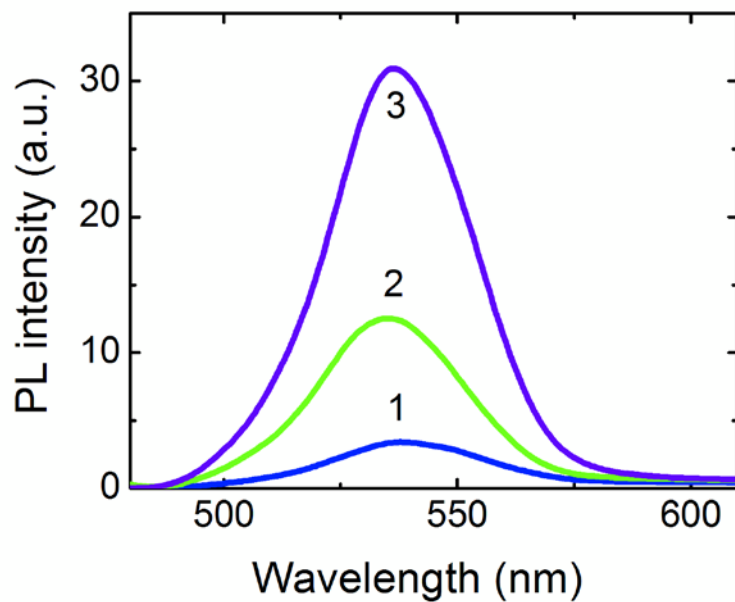


Fig.4. PL spectra of porous glass samples with CdSe/ZnS QDs: (1) is the spectrum of the sample after 20 min exposure to ammonia vapor; 2 and 3 are the spectra from the sample after 7 days of storage under ambient conditions and after 10 min vacuum degassing at a pressure of ~ 1 torr, respectively.