Interaction of ammonia vapors with CdSe/ZnS quantum dots in porous matrices

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Ammonia is a one of the most wide spread compounds in the nature and industry. At the same time ammonia vapor can be harmful for human health [1]. Therefore, monitoring and detection of the ammonia vapor are very actual and important problem. One way of detection of different compounds is the use of specific molecules or particles that can change their properties due to interaction with the analyte. In particular, using of optical technologies enable ones to detect of ammonia with high sensitivity [2].

Nowadays a colloidal synthesis of a new class of inorganic luminophore, semiconductor quantum dots (QDs), is well developed [3]. QDs possess some helpful properties, the most important of them is size-dependence of QD optical characteristics (absorption and luminescence). This property along with a high extinction, a high quantum yield of luminescence, a high photo- and chemical stability allows them to compete with conventional luminophores. Combining the features of the semiconductor QDs with specific porous matrices that can concentrate analyte species allows getting a new class of luminescent sensor system with the high sensitivity and a broad dynamic range.

Here we discuss two types of porous matrices impregnated with CdSe/ZnS quantum dots, which can change their luminescent properties due to interaction with ammonia vapor. In present study bright luminescent hydrophobic CdSe/ZnS quantum dots were embedded in terephthalate track pore membranes (TM) with pore size of 500 nm and in a borosilicate porous glass (BG) with pore size of 17 nm. The systems are shown in Figure 1. The CdSe/ZnS quantum dots embedded in the TM are quasi-isolated and possess optical properties like those in QD colloidal solution [4]. For QDs embedded in the porous glass, the steady-state absorption and luminescence spectra also coincided with those in colloidal solution, however an average luminescence decay time became one and a half times longer, 20 ± 2 ns *vs* 32 ± 2 ns. We propose that the adsorption of quantum dots on the inner surface of pores decreases a number of QD surface defects responsible for nonradiative deactivation of the QD excited states. This results in an increase in the luminescent average decay time of QDs. The optical properties of QDs embedded in the porous glass indicates that in this matrix QDs are isolated and do not interact with each other.

In order to investigate an interaction of the ammonia vapors with our samples we have incubated them in a hermetic box of 16 ml volume with 5 µl drop of 10% ammonia water solution on its bottom. Since samples did not contact with the drop of the ammonia solution the QDs interacted only with ammonia vapors with concentration of $\sim 1.7 \cdot 10^{-3}$ mol/l. We have observed that in both matrices the interaction of ammonia vapors with QDs leads to significant quenching of their luminescence and shortening their luminescent decay time (see Figure 2). We propose that in both matrices ammonia molecule form a complex with QD via coordination onto surface Zn ion of the QD shell similar to the QD/pyridine complexes [5].

Figure 2 shows that the luminescence response of QDs exposed to ammonia vapors differs for the TM and the BG samples. The dependence of QD luminescence decay on the time of interaction with ammonia vapors clearly shows that an adsorption of one ammonia molecule onto QD surface does not lead to complete quenching of this QD. It means that the degree of luminescence quenching of QD depends on stoichiometry of the QD/ammonia complex, i.e. on the number of ammonia molecules per QD. We assume that passivation of QDs in the BG matrix leads to a significant decrease a number of Zn ions on QD surface that can serve as coordination centers for ammonia. Therefore, this can lead to a decrease of the degree of luminescent quenching of QDs as compared with the TM matrix.

It should be noted that formation of QD/molecules complexes is often accompanied with an appearance of new nonradiative channels of deactivation of excited state of QDs, which compete with the energy or charge transfer in these complexes. Usually a nature of these channels is not clear. In the complexes of CdSe/ZnS QDs with ammonia molecule the energy or charge transfers are excluded. So, an effective quenching of QD luminescence in these complexes should be explaining by other reasons. A mechanism of the luminescence quenching and the reduction of QDs decay time is not quite clear at the moment. We believe that in the complexes of CdSe/ZnS QDs with ammonia molecule the reasons of luminescence quenching of QDs could be an energy transfer from QD to NH-vibration of ammonia molecule [6] or an appearance of new local sites on the QD surface at the points of coordination of molecules [7], which can serve as electron traps. Additional studies are now in progress.

The reusability is a one of important characteristics of any sensor elements. In our samples we found that full recovering the luminescent properties of QDs exposed to ammonia vapors took place after 10 min vacuum degassing at ~1 torr pressure. After complete cycle of adsorption/desorption of the ammonia molecules on the surface of CdSe/ZnS QDs embedded in the matrices we have examined the ability of QDs to adsorb a new portion of ammonia molecules. Repeated forming the QD/ammonia complexes under the same conditions showed that QDs keep their photophysical properties after interaction with the ammonia molecules. Therefore, this system could be used as reusable sensor on the ammonia vapors.

The dependence of luminescent properties of QDs on number of ammonia molecules adsorbed on their surface opens up the possibility to use the CdSe/ZnS quantum dots embedded in the porous matrices as a sensor element for quantitative detection of the ammonia vapors.

References

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Figures

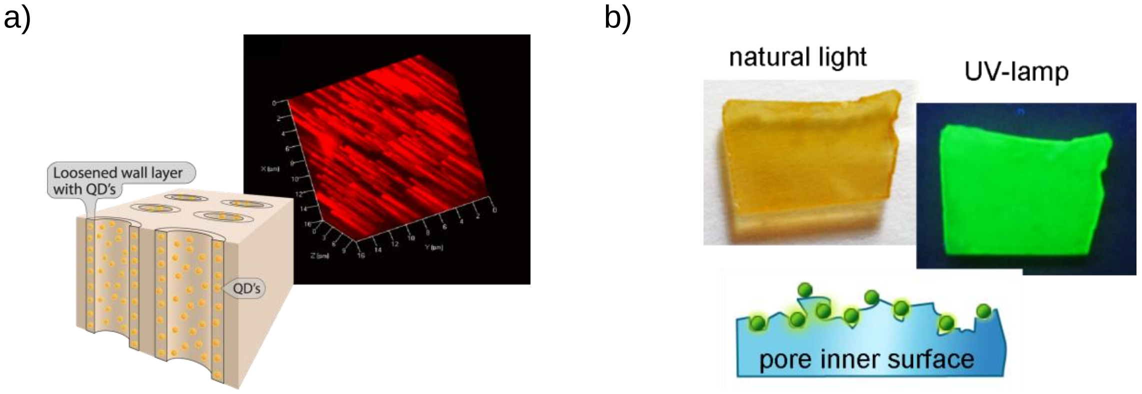

Figure 1. (a) QDs in the terephthalate track pore membrane, sketch and the 3D confocal luminescent image. (b) QDs in the borosilicate porous glass, sketch and the photos.

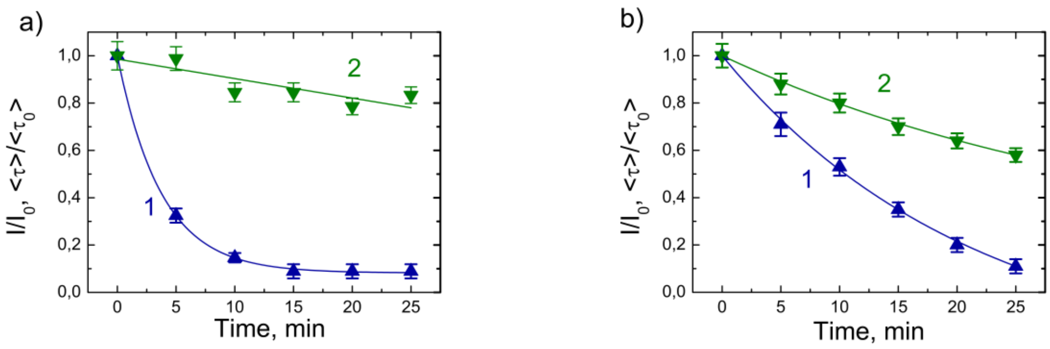

Figure 2. Dependencies of luminescence intensity (1) and decay time (2) of the CdSe/ZnS QDs embedded in the porous matrices: a) The terephthalate track pore membrane. b) The borosilicate porous glass.