Sensing and photocatalytic activity of zinc sulfide quantum dots based on charge transfer process to analyte molecule

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Abstract. We demonstrated the efficient charge transfer between manganese doped zinc sulfide quantum dots (QDs) and an analyte molecule, methane or methylene blue dye, by means of photoluminescence properties of ZnS QDs. In the presence of methane QDs are found to exhibit non-uniform increasing of luminescence intensity due to specific charge transfer from analyte to QD defect states. It is revealed that charge transfer leads to destruction of methylene blue dye molecule which makes possible to use the QDs for organic dye removal in aqueous solution. The limit of methane detection is 100 ppm. The photocatalytic rate of methylene blue degradation is 0.033 s⁻¹ which is almost two orders higher than Degussa P25 rate.

1. Introduction

Semiconductor nanocrystals that are quantum confined in three dimensions, or quantum dots, have received much attention as low-cost active materials for highly efficient optoelectronic devices [1] and solar-to-fuel conversion applications, namely, photocatalysis, because of their unique size-dependent properties and cost-effective solution processing. These applications involve QDs as charge separation centers, and a critical and fundamental step is the electron or hole transfer from photoexcited QDs to analyte molecule acting like electron or hole acceptors through a nanoscale interface [2]. A lot of emission centers in QDs result in strong dependence of electron transfer process inside the QD to its surface states, which makes QDs very attractive for implementation in luminescent sensors based on electron transfer process from QD to analyte molecule. Depending on specific of QD-to-analyte charge transfer analyte presence can initiate enhancement or quenching of QDs luminescence [3]. For example, if the QD is close to a molecule exhibiting a LUMO level at lower energy than that of the QD conduction band edge, a photoinduced electron transfer from the QD to the electron acceptor can occur and the luminescence of the QD is consequently quenched. On the other hand, in the presence of an electron donor exhibiting a HOMO level that is less positive than the valence band edge, electron transfer from the donor to the holes associated with the valence band occurs resulting in decreasing of non-radiative transitions in QDs and, correspondingly, enchanting QD luminescence.

Due to high redox nature of QDs such charge transfers took place only for analyte molecules with strong chemical bond. Otherwise, photogenerated charge carriers can destruct analyte chemical bonds leading to photoinduced (or photocatalytic) degradation of analyte molecule [4].
Here we report the successful realization of photoinduced charge carrier transfer between QDs and analyte molecule. Depending on analyte nature charge transfer results in formation of luminescent sensor response in analyte presence or photocatalytic degradation of analyte molecule.

2. Materials and Methods

The quantum dots were prepared using aqueous solutions of zinc and manganese acetates (Zn/Mn ratio from 0.01/0 to 0.01/0.0004 mol/l), glutathione, sodium hydroxide and sodium sulfide. Under vigorous stirring, the solution of zinc/manganese acetate was introduced into a solution of glutathione. Then a solution of NaOH was added and stirred in a water bath at 80 °C for 30 minutes. A solution of sodium sulfide was added dropwise to the mixture for 30 minutes. The resulting mixture was heated at 90 °C for an hour.

Fluorescence spectroscopy study was performed with Fluorolog 3 fluorescence spectrometer (Horiba, Japan) equipped with continuous 450 W Xenon lamp source and pulse 150 W Xenon lamp source. Study of sensor characteristics was carried out in a special sealed cell (filled with aqueous QDs solution) coupled with spectrometer sample chamber. The methane level was preset by bubbling 10% argon-methane gas mixture with a flow rate of 100 ppm of methane per minute.

The photocatalytic degradation of methylene blue (MB), a typical conjugated aromatic dye, was chosen as a model reaction to evaluate ZnS:Mn$^{2+}$ photocatalyst activity. MB is a weakly luminescent dye with two PL excitation (PLE) bands at 1.85 and 4.27 eV, PL maximum is close to 1.81 eV. The energy of the exciting photons was 4 eV that, on the one hand, corresponds to the ZnS QD band gap, and on the other hand, it ensures the excitation of the MB luminescence. Taking into account that PL intensity of methylene blue is directly proportional to its concentration, the simultaneous excitation of the QDs and the dye allowed us to observe the process of dye degradation in real time by decreasing the PL band at 1.81 eV.

The rate of photocatalytic decomposition was determined as

$$-\ln\left(\frac{C}{C_0}\right) = kt$$

where $C_0$ is the initial MB concentration; $C$ is the MB concentration at time $t$, and $k$ is the rate of catalytic decomposition [5].

3. Results and Discussion

Fig. 1 shows the room temperature PL spectra of Mn$^{2+}$-doped ZnS QDs under 4 eV excitation.

![Figure 1. PL spectra of Mn$^{2+}$ doped (0.05 at.%) ZnS QDs in glutathione. The solid line shows the resulting curve, the dashed lines indicate Gaussian components.](image-url)
In undoped ZnS QDs the only one emission band at 3.1 eV is present. However, all the doped samples show broad emission band with maxima at 3.1 and 2.11 eV. Deconvolution of emission band at 3.1 eV by Gauss functions revealed three luminescence centers corresponded to interstitial zinc ions (I_{Zn}, E_{max} = 2.97 eV), sulfur vacancies (V_S, E_{max} = 2.7 eV) and surface defects (D_{surf}, E_{max} = 2.5 eV). Such luminescence centers are well-known for ZnS QDs and are in agreement with other reports [3]. Emission band at 2.11 eV is related to ^4T_1→^6A_1 transition within 3d configuration of Mn^{2+} ion. Increasing of Mn^{2+} concentration leads to the PL intensity decreasing at 3.11 eV band. The intensity of Mn^{2+} related emission increases up to dopant concentration of 2 at.% after that concentration quenching occurs. Because both ZnS- and Mn^{2+} related PL bands took place, one can conclude that Mn^{2+} ions are incorporated in ZnS crystal lattice [3, 6].

To reveal the possibility of sensor response realization due to QD-to-analyte energy transfer a methane as an analyte sample was chosen. Methane has 4 bonding and 4 antibonding molecular orbitals (MO) with energy levels varies from -18.79 eV to 3.9 eV. The four bottom methane MOs are all occupied and have energy lower than the non-bonding energy level (0 eV). The highest four methane molecular orbitals are empty, so it is possible to put an electron in one of these MOs, resulting in energy transfer. For studied ZnS:Mn QDs this process can occur by direct electron transfer to methane LOMO level from QD conduction band or through electron transfer from QD bandgap intrinsic defects including Mn^{2+} energy levels.

Under exposure even relatively low methane concentrations QD luminescence change significantly (Fig. 2). Bubbling by 100 ppm of methane through QD solution leads to increasing of both ZnS- and Mn^{2+}-emission bands. Herewith, ZnS-related PL band shifts to the region corresponded to sulfur vacancies and interstitial zinc ion emission. Mn^{2+} PL band, as well as V_S and I_{Zn} bands, demonstrates ≈1.5-2 times amplitude increasing whilst D_{surf} emission band increases its amplitude up to 4 times (Fig. 4).

![Figure 2](image1.png) **Figure 2.** PL spectra of Mn^{2+} doped (0.05 at.%) ZnS QDs under 100 ppm methane exposure (black curves) compared to initial PL spectra (grey curves).

![Figure 3](image2.png) **Figure 3.** Intensity of QDs emission bands under exposure to different methane concentrations. Intensities was normalized to Mn^{2+} band at initial state.

Considering the fact that QD solution was bubbled by argon-methane gas mixture the observed luminescence increase may be caused by argon presence too. To exclude QD response to argon exposure an optical response to pure argon exposure of the same concentration was investigated. The 2 times increasing for all PL bands was detected. This fact allows us to suggest that QD sensor response to argon-methane gas mixture exposure involves two processes: (I) QD passivation by argon molecules resulting in gradual luminescence increasing for all emitted centers; (II) specific reaction of QD surface to methane molecules resulted in selective sensor response formation.

It was found that the photocatalytic decomposition rate of methylene blue depends on the concentration of the Mn^{2+} (Fig. 4). For manganese-doped ZnS QDs, the decomposition of the most
MB molecules occur within 200 seconds after the onset of irradiation. At the same time, a gradual increase in the dopant concentration leads to a reduction in the degradation time of MB. A minimum time achieved is 120 s for the sample with 0.125 at.% of Mn$^{2+}$. A further increase in the manganese concentration leads to an increase of photocatalytic decomposition time of methylene blue, presumably due to a change in the recombination rate of photoexcited charge carriers noted by a number of authors [7] and which is of great importance in the photocatalytic material development.

![Figure 4](image_url) Photocatalytic degradation rate of MB in the presence of ZnS:Mn$^{2+}$ QDs in comparison with commercial photocatalyst Degussa P25.

The deviation from the linear dependence of the dye concentration logarithm can be explained as the processes of sorption of the dye molecules by the surface of the quantum dot. The efficiency of photocatalytic decomposition is affected by both the sorption probability of closely located MB molecule by the surface of the quantum dot and the rate of photocatalytic decomposition. Thus, at a sufficiently high concentration of the MB (at a time from 0 to 75 s), the sorption and photocatalytic decomposition processes take place quite rapidly. With a decrease in the concentration of methylene blue, the probability of a close location of the quantum dot and the dye molecule decreases that causes non-linear dependence of dye concentration logarithm in 100 s.

A comparison of the obtained results of the photocatalytic activity of ZnS:Mn$^{2+}$ QDs with the available passport data of the reference photocatalyst Degussa P25 demonstrate the high efficiency of proposed nanocrystals.

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