Nanoscaled Science and Engineering for Sensing: Quantum Dots Fluorescence Quenching for Organic NO_2 Sensing

S. Nieto*, Alberto Santana*, R. Delgado*, S.P. Hernandez*, R.Thomas Chamberlain**, Richard Lareau** and Miguel E. Castro*

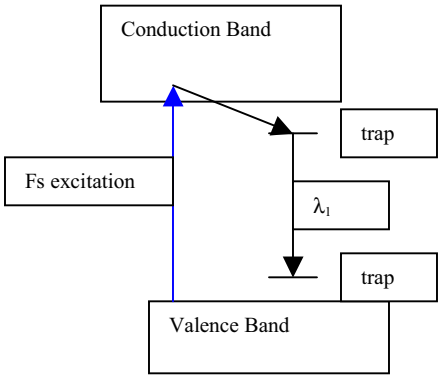
*Chemical Imaging Center, The University of Puerto Rico at Mayaguez, Mayaguez, Puerto Rico 00680, mcastro@uprm.edu
** Visiting Scholars, Federal Transportation Security Administration, Federal Aviation Administration Technical Center, Atlantic City, New Jersey, 08405

ABSTRACT

We report on femtosecond laser off-resonance excitation of quantum dots-TNT assemblies in solution. The fluorescence emission from quantum dots shifts toward lower wavelengths and the relative peak intensity decreases with the amount of TNT added to solutions of the dots. A charge transfer mechanism based on charge injection from the photoexcited electrons in the TNT into the conduction band of the nanoscaled semiconductor is proposed to account for the observed results.
Keywords: femtosecond excitation, quantum dots-TNT assemblies, TNT sensing, nanoscaled sensors, charge transfer

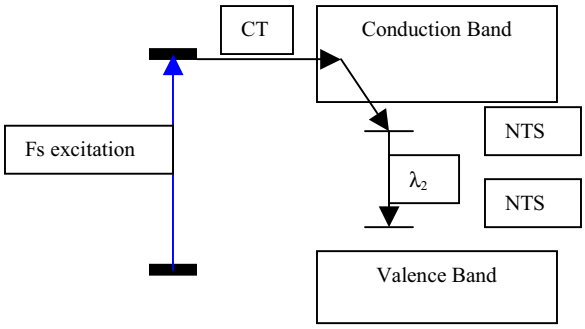
1 INTRODUCTION

Detection of trace amounts of explosive materials is an important task with a broad range of implications, from national security to the cleanup of demilitarized installations. Nanotechnology is ideally suited to serve our Nation needs by providing new materials and methods that can be employed for trace explosive detection.[1-4] Fluorescent nanoparticles, like nanoscaled semiconductors or quantum dots (QD), have the potential to be employed in trace explosive detection in a number of environments. Variations in the particle fluorescence wavelength may serve as a tool to the detection of trace amounts of explosive chemicals. In the ideal case scenario, a QD emitting light with wavelength λ_1 will change its emission line to λ_2 upon bonding to an explosive molecule, as illustrated in schemes 1 and 2 below.



Scheme 1: Typical fluorescence mechanism from QD.

In typical QD, fluorescence electrons and holes are created following excitation with light of energy equal or larger to the band gap or energy difference between the valence and conduction band. Photo-excited electrons in the conduction bands are energetically relaxed to states introduced by traps in the particle. Luminescence emission results from relaxation of electrons from trap states into the valence band or to other empty "trap states".



Scheme 2: Proposed charge transfer (CT) or new trap state (NTS) model for the changes in fluorescence emission of QD-TNT assemblies.

We report here on the effect of 2,4,6 trinitrotoluene (TNT) on the fluorescence emission of zinc sulfide (ZnS) protected cadmium selenide (CdSe) quantum particles. The fluorescence is excited off-resonance with respect to the quantum dots, but close to the absorption band edge of the TNT. This is proposed to result in charge transfer (CT) process between TNT and the quantum dots and/or the involvement of new trap states (NTS) in the fluorescence emission of the dots, as illustrated in scheme 2.

2 EXPERIMENTAL

Solutions of CdSe quantum dots in toluene were purchased from Ocean Optics. The dots are between 2 and 12 nm in diameter. The CdSe core shell is protected by a ZnS layer. The 800 nm line from a Spectra Physics femtosecond laser system operating at a repetition rate of 1 kHz was feeded into a Spectra Physics Wave Generator were it was frequency double by sum frequency methods to provide the 400 nm line employed to excite the fluorescence in the quantum dots. Solutions containing the quantum dots were placed in a standard quartz cell. TNT was added with the use of a calibrated micropipette from a 1 ppm TNT in toluene solution. The fluorescence was collected at 90° degrees with respect to the incident radiation and measured with a JY Triax 550 spectrograph equipped with a UV-visible CCD.

3 RESULTS

Representative fluoresce spectra of quantum dots in toluene and quantum dots exposed to various amounts of the TNT in toluene solution are displayed in figure 1. The fluorescence of the QD in toluene solution used to collect the results displayed in figure 1 is centered at 534 nm. The position of the peak is independent of the amount of toluene added, as verified in independent measurements. The peak shifts toward lower wavelengths and the peak area decreases with the amount of TNT added. So far, we have observe this trend when the QD are exposed to the TNT solution. Independent measurements revealed that the position of the peak does not change upon the addition of highly reactive species, like alkyl thiols or carboxylic acids.

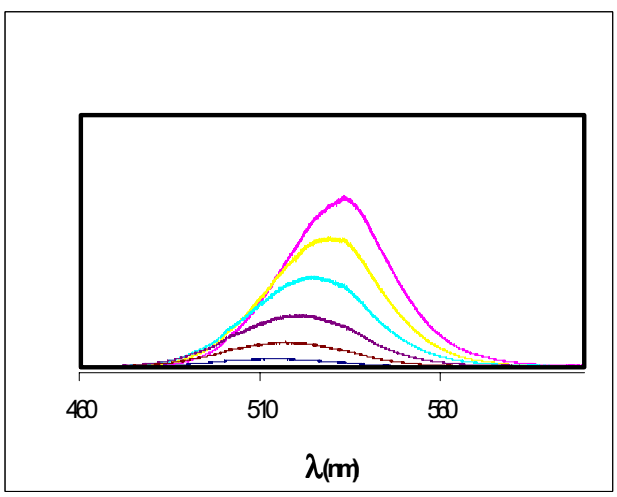


Figure 1: Fluorescence spectra of CdSe/ZnS QD exposed to 0, 5, 25, 50, 100 and 300 mL of a 1 ppm TNT in toluene solution.

Figures 2 and 3 summarizes results from quantitative analysis of peak intensities and maximum fluorescence wavelength as a function of the amount of added TNT to solutions containing the QD employed for the measurements described on figure 1. The fluorescence relative peak area decreases with the amount of added TNT to the solution. This decrease in peak area is not related to a dilution effect, as verified by independent measurements performed on QD exposed to volumes of toluene free of TNT. Such measurements showed that the fluorescence intensity varied proportional to the concentration of the QD in solution. We conclude then, based on the results presented in figures 1 and 2, that the fluorescence of the QD is quenched by the added TNT.

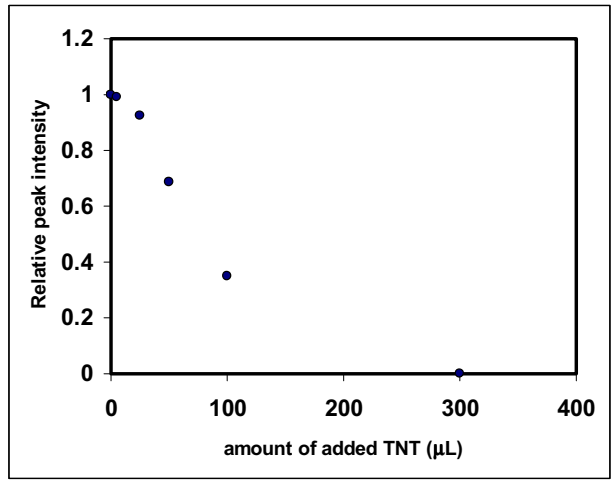


Figure 2: Fluorescence relative peak intensity as a function of the amount of TNT in toluene added to a solution of QD in toluene.

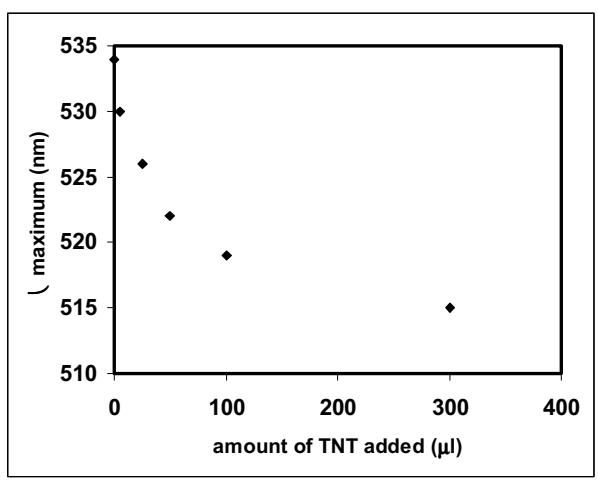


Figure 3: Fluorescence maximum wavelength (nm) as a function of the amount of TNT added (µL).

The fluorescence maximum wavelength also experiences marked changes upon the addition of TNT to the QD in toluene solution. These are summarized in figure 3. The fluorescence maximum wavelength shifts toward lower energies with increasing the amount of TNT added to the QD in toluene solution. We take this result as evidence for strong interactions among the TNT molecules and the QD.

QD emitting at other wavelengths were also studied. The general trend presented in the previous paragraphs regarding the effect of TNT on the fluorescence maximum wavelength and relative peak intensity was also observed. For instance, the fluorescence maximum of a QD that emits at 567 nm was shifted to 558 nm upon the addition of 100 µL of a 1 ppm TNT solution. The relative peak intensity was observed to decrease by 30 % in the above case. Fluorescence quenching was more marked in a QD that emits at 605.9 nm. In that case, the fluorescence maximum emission wavelength shifted to 598 nm and the fluorescence relative peak intensity decreased by 92 % upon the addition of 50 µL of a 1ppm TNT solution. Thus the results are consistent with a quenching in the fluorescence of the QD and a change in the fluorescence mechanism of the QD upon the addition of TNT.

4 DISCUSSION

The results presented here are consistent with extensive quenching and a change in the fluorescence emission of QD by TNT. The results prove that the QD may find applications in TNT sensing from observations of a second wavelength (λ_2), distinctive from the emission wavelength (λ_1) of the QD in the absence of the TNT.

The changes in the maximum fluorescence wavelength as a function of added TNT are major finding of the work presented here. The changes may be accounted for by a charge transfer mechanism (CT) of TNT electrons into the conduction band of the QD or by the appearance of new "trap states" (NTS) that are not present for the QD, as presented in schemes 1 and 2. Alternatively, a mechanism involving both, CT and NTS, may be needed to explain the observed shifts in the fluorescence of the QD as a function of added TNT.

The arguments presented above assume that the TNT has no effect in the size of the QD. Particle size plays an important role in the eavelength emission of quantum dots, as it is well known that the band gap energy (ΔE) is inversely proportional to the diameter of the particle. If TNT induces a change in the size of the QD, then, ΔE will change and, consequently, the fluorescence emission wavelength. Independent UV-visible absorption measurements (not shown) failed to show a change in the leading edge of the absorption spectra of the QD upon the addition of TNT, indicating that the results presented here can not be explained by a mechanism that involves a change in the size of the particle. In view of the above arguments, we believe that either a CT and/or NTS mechanism may be responsible for the effect of TNT in the fluorescence emission of the QD. Further work is needed to clearly establish the mechanism of fluorescence of the QD in the presence of TNT.

5 ACKNOWLEDGEMENT

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