On the Use of Core-Shell Type Semiconductor Nanocrystals as Sensors

Jens U Sutter, Olaf J Rolinski & David JS Birch
Photophysics Group, Department of Physics, John Anderson Building, University of Strathclyde, Glasgow G4 0NG, Scotland, UK
djs.birch@strath.ac.uk

Abstract
Here we describe progress towards our objective of non contact transition metal ion sensing. Semiconductor nanocrystals show complex photophysical properties and require a very careful setup of the measurement parameters. Under these conditions they allow for very high resolution sensing of ions.

1. Why look for new fluorescent sensors?
Fluorescent imaging has over the last two decades undergone rapid development with the discovery and exploitation of the fluorescent proteins and further development of organic fluorophors. While fluorescent proteins provide exciting opportunities, fluorescence stability remains a

2. Brightening and Quenching
Further investigation of the fluorescence characteristics of commercially available quantum dots showed that the fluorescence lifetime is a function of the excitation energy. Quantum dots QDots525® (INVITROGEN) are immobilized in gel matrix and excited at different energy levels. The fluorescence lifetimes as well as the fluorescence intensity change with the previous excitation energy. This effect is seen in other types of core-shell type semiconductor nanocrystals as well. Quenching a quantum dot as brightness is fully reversible.

3. Non-Contact Ion Sensing
We aim to achieve non-contact interaction between sensor and target ion by means of Förster Resonance Energy Transfer (FRET) [2]. In that case we should be able to describe the fluorescence according to a Förster formalism with the fluorescence decay given by:

\[ I(t) = I(0) \exp(-t/\tau_g) \]

With \( \tau_g \) being the transfer coefficient between donor and acceptor, defined as:

\[ \gamma = \frac{C_A}{C_g} \]

\( \gamma \) is the concentration of the acceptor and \( C_g \) is the critical acceptor concentration as calculated from the overlap integral between donor emission and acceptor absorbance.

Fitting our data to FRET kinetics showed good agreement between measurement and model and suggested the interaction to be without contact between sensor and target.

4. Transition Metal Ion Sensing
Transition metal ions like copper and nickel play an important role in biology as nutritional micronutrients as well as important ligands in proteins e.g. manganese in the photosystem II of plant cells or copper in the regulation of intracellular transport [3]. Sensing transition metal ions in biological systems by chemical methods proves to be difficult for concentrations are small and chemical sensing interferes with the very process one desires to monitor.

Using a sol gel to immobilize the quantum dots, we obtain a matrix which can be used to perform with ions solution to measure the effect of quantum dot - ion interaction. QDot800 provides a suitable sensor for copper ions.

Are we looking at non-contact interaction?
We analyse the fluorescence lifetime of the quantum dots. The fluorescence decay of the quantum dot can be described by a single exponential decay. Upon addition of copper we observe a Förster type quenching, suggesting indeed non-contact interaction via resonance energy transfer.

5. Quo Vadis?
Biosensing: Non Contact Ion Sensing
We have shown that semiconductor nanocrystals demonstrate kinetics consistent with non contact sensing of single transition metal ions. This technique will open exciting possibilities for ion sensing in biological samples with minimal interference with the target.

Biotracking: Photo-activated quantum dots for protein and molecule tracking
It has been shown that fluorescent proteins which can be activated by excitation light greatly enhance the possibilities of protein tracking in cells [1]. The time of observation though is short due to photodamage to the fluorophore. We propose using the unique characteristics of semiconductor nanocrystals to develop a photo-activated quantum dot for greatly enhanced observation times.

Information Technology: Optical switches
Understanding and utilizing the changes in fluorescent characteristics in quantum dots might pave the way towards an optical storage device in information technology.

References:
[3] Li J, Elman A, Bred CG. “Regulation of Copper-Dependent Endocytosis and Vascular Degradation of the Yeast Copper Transporters, Ctx1p, by the Rsp1p Ubiquitin Ligase.” Traffic. 2007