Reliable photoluminescence quantum yield measurements in the near-infrared spectral region

S. Hatami, C. Würth, U. Resch-Genger, BAM Federal Institute of Materials Research and Testing, Berlin, Germany (February 2013)

Application Note

Within the last years, semiconductor quantum dots (QDs) with their unique size-tunable optical properties, their flexible excitation, and their narrow and symmetric emission bands are increasingly applied as fluorescent labels and sensors and as active components in optical devices [1].

Especially attractive for many applications in the life sciences like cellular and in vivo fluorescence imaging are QDs that emit in the near-infrared (NIR) and infrared (IR) region like CdTe, CdHgTe, HgTe, PbS and PbSe due to their favorably high photoluminescence quantum yields (QY) compared to the QY values of any other chromophores at emission wavelengths above 900 nm [2].

The characterization of the performance of these NIR and IR QDs requires reliable methods for the determination of QY under application-relevant conditions [2,3]. For often performed relative optical measurements, quantum yield standards with precisely known QY are mandatory. The performance of such measurements are hampered by the lack of reliably assessed QY standards for the NIR and IR [4]. Moreover, only very few organic dyes emit above 1000 nm and their QY values are typically below 0.01 as found e.g. for IR26, the commonly used standard for relative QY measurements of IR-emissive QDs [2].

Accordingly, the QY of QDs in this wavelength region must be determined absolutely. This can be achieved with an integrating sphere setup where all photons absorbed and emitted by the sample can be measured without the need for a standard, see equation 1, with N_{em} and N_{abs} equaling the number of emitted and absorbed photons. This presents the most efficient approach to obtain photoluminescence QYs.

$$QY = \frac{N_{em}}{N_{abs}} \qquad (1)$$

This encouraged us to design an integrating sphere setup for the absolute measurement of QY values in the spectral range of 600 nm to 1700 nm and to develop procedures for the relative and absolute determination of QY of emissive materials in this wavelength region. The main components of our setup are a continuous light source, an integrating sphere and from Andor Technology a Shamrock SR-303i-B spectrograph coupled to an iDus InGaAs 1.7 µm photodiode array (DU491A-1,7) (Figure 1). The wavelength-dependent spectral responsivity of the detection system that presents one of the main sources of uncertainty of absolute quantum yield measurements, was determined with two different calibrated light sources.

Figure 1: The IDus InGaAs 1.7 µm on a Shamrock SR-303i spectrograph.

The measurement of absolute QY of dilute solutions of organic dyes and QDs according to eq 1 with our integrating sphere setup consists of the following steps: (i) determination of the of the transmitted excitation light and the emitted light of the sample and a blank

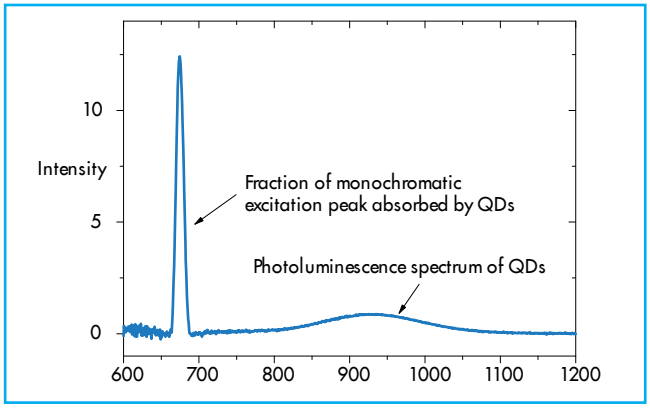

Figure 2: The quantum yield of the QDs is the ratio of the number of emitted photons per number of absorbed photons.

S. Hatami, C. Würth, U. Resch-Genger, BAM Federal Institute of Materials Research and Testing, Berlin, Germany (February 2013)

(solvent-filled cuvette; under identical measurement conditions (e. g., excitation wavelength, tempe-rature etc.), (ii) data evaluation including choice of the excitation and emission wavelength region used for signal integration and spectral emission correction, and (iii) calculation of the fluorescence quantum yield according to eq. 1. This is illustrated in Figure 2, showing the corresponding spectra measured with our integrating sphere-InGaAs ensemble.

Acknowledgments
We thank the group of Prof. Dr. Alexander Eychmüller for supplying the samples for this study. Financial support from the Deutsche Forschungsgemeinschaft (DFG grant RE-1203/12-1) is gratefully acknowledged.

References
[1] U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, T. Nann, Nature Methods 5 (2008) 763.
[2] O. E. Semonin et.al., The Journal of Physical Chemistry Letters 1 (2010) 2445.
[3] M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmüller, U. Resch-Genger: Anal. Chem. 81 (2009) 6285.
[4] C. Würth, J. Pauli, C. Lochmann, M. Spieles, U. Resch-Genger, Anal. Chem. 84 (2012) 1345.

Contact
Dr. Ute Resch-Genger
Head of division 1.10, Biophotonics
BAM Federal Institute of Materials Research and Testing
Richard-Willstaetter-Straße 11
D-12489 Berlin
Phone: +49 30 8104-1134
E-mail: ute.resch@bam.de

http://www.bam.de/de/kompetenzen/fachabteilungen/abteilung_1/fb110/index.htm