On critical artifact present in standard quantum yield methodology

Katerina Dohnalova* and Bart van Dam

Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH, Amsterdam, The Netherlands

* presently Katerina Newell, email: k.newell@uva.nl

Photoluminescence quantum yield (QY) methodology offers seemingly simple and robust way of assessing the emission efficiency in light emitting materials, such as dyes or semiconductor quantum dots (QDs). Using already standardized and widely used integrating sphere (IS) technique, it has been accepted as the standard methodology even in the industry. Here we show, for the first time, that the very same QY methodology suffers from a critical artifact, independently of the specific implementation, as soon as sample's absorption is compared to a blank reference. This artifact shows as QY dependence on absorption below certain absorption threshold - The lower the absorption, the more are the QY values underestimated. This happens as soon as the uncertainty in the number of measured absorbed photons is approximately 1/10th of the absorption of the sample - e.g. for uncertainty in measured number of absorbed photons of 1%, samples with absorption below 10-15% are already affected and underestimation in QY value is more than 200%. This effect is illustrated in Figure 1a, where excitation energy dependence of QY of Rhodamine 6G (R6G) is plotted for several different concentrations. Absorption is hence changed by both, concentration and excitation wavelengths. In Figure 1b is shown the same QY data, plotted this time against absorption itself, exhibiting a unified trend. The same absorption dependent QY curve is obtained for other materials, such as Silicon and CdSe QDs and with different experimental setups, proving that this artifact is material and setup independent.



Figure 1. (a) Experimentally determined QY as a function of the excitation wavelength for different concentrations of R6G in ethanol. Dashed black lines serve as guides to the eye, the solid lines represent the single-pass absorption of the highest and lowest concentration sample (right axis). For comparison with literature, the QY values as determined by Faulkner et al. (Ref 1) for two concentrations are added (red). (b) QY values from (a) plotted versus the single-pass absorption to illustrate the dependence of QY on absorption. Blue points represent QY values obtained for different

concentrations under 380 nm excitation wavelength. Red points are again data from Faulkner et al. (Ref 1). The vertical dashed line indicates the critical absorption, A_{crit} , below which QY is underestimated.

In general, we conclude that every study, where QY of samples with different absorption is compared, is affected. These are very common experimental conditions, which means that this artifact has been influencing number of published studies (e.g. Refs 2-6), rendering their conclusions flawed. Using our theoretical simulations,⁷ we suggest modified QY methodology with an additional calibration protocol, which needs to be used in every case when QY of samples with varying absorption is evaluated and interpreted. In Figure 2 are shown examples of QY dependencies on excitation wavelength (and hence indirectly on absorption) before (Figure 2a) and after (Figure 2b) correction for the presented artifact. Correction removes all apparent excitation wavelength dependencies or makes them less pronounced.



Figure 2 - QY of Rhodamine 6G (black and gray), SiQDs (red) and CdSe QDs (blue) versus excitation wavelength, before (a) and after (b) correction for the QY methodology artifact. Different symbols represent different sample concentrations. After correction, the QY of the R6G and Si QDs is constant and independent of the sample's concentration. Part of the excitation and concentration dependence of the QY of the CdSe QDs persists after correction, potentially related to the ligands on the surface.

[1] D. O. Faulkner et al., Laser Photonics Rev. 6 (2012) 802.

- [2] D. Timmerman et al., Nature Nanotechnology 6 (2011) 710.
- [3] M. Greben et al., J. Appl. Phys. 117 (2015) 144306.
- [4] M. L. Mastronardi et al., Nano Lett. 12 (2012) 337.
- [5] J. B. Miller et al., ACS Nano 6 (2012) 7389.
- [6] W. Sun et al., Adv. Mater. 27 (2015) 746.
- [7] B. van Dam et al., (2017) <u>arXiv:1711.06200v1</u> [physics.ins-det]