Photoelectrochemistry of layers of ZnS:Mn nanocrystals

J. F. Suyver, A. Meijerink and J. J. Kelly
Debye Institute, Physics and Chemistry of Condensed Matter, Utrecht University, PO Box 80 000,
3508 TA Utrecht, The Netherlands
E-mail address: suyver@phys.uu.nl

The broad research interest in nanosized materials is justified by the many applications that would benefit greatly from having these materials as active components [1]. Potential applications include: next generation of computer chips, where the drive for smaller and smaller structures is most obvious; biological labeling applications, where the semiconductor nature of these materials ensures long stability; and electroluminescent materials, where the stability (compared to organic emitters) and the tunability of the emission are important points.

From a production point of view, the chemical synthesis of the nanocrystals which can usually be scaled up without much difficulty, would be preferable to physical deposition. The wet chemical synthesis of various (doped) nanocrystals has been studied extensively in the last years. Recently, control over the size and luminescence characteristics of chemically prepared ZnS:Mn^{2+} nanocrystals was shown [2]. These nanocrystals are dip-coated on a transparent conductor such as ITO or TFO. After a mild temperature treatment (200 ^{o}C), to ensure layer stability, these electrodes were suitable for (photo)-electrochemical measurements.

A fascinating result is shown in Figure 1, in which both an anodic and a cathodic photocurrent are observed. Although the currents are quite small, they do confirm the nanoparticulate character of the electrodes [3]. After a discussion of this result, the presentation continues with the potential dependence of the photoluminescence of these electrodes. As is shown in the inset of Figure 2, the spectrum is dominated by the Mn^{2+} emission (~600 nm) and the ZnS defect related emission (~430 nm) is rather weak.

Figure 2 shows that the luminescence intensity is almost constant over a broad potential range. However, a small hysteresis is present (roughly 4% of the total signal intensity). A set of chemical reactions that might be involved is proposed. The long-term stability of the electrodes is not very good, as was ascertained from SEM images. This fact will be explained by the data shown in Figure 2.

Finally, attempts to measure electroluminescence in an aqueous electrolyte are briefly discussed and suggestions for obtaining a working electroluminescent system are presented.

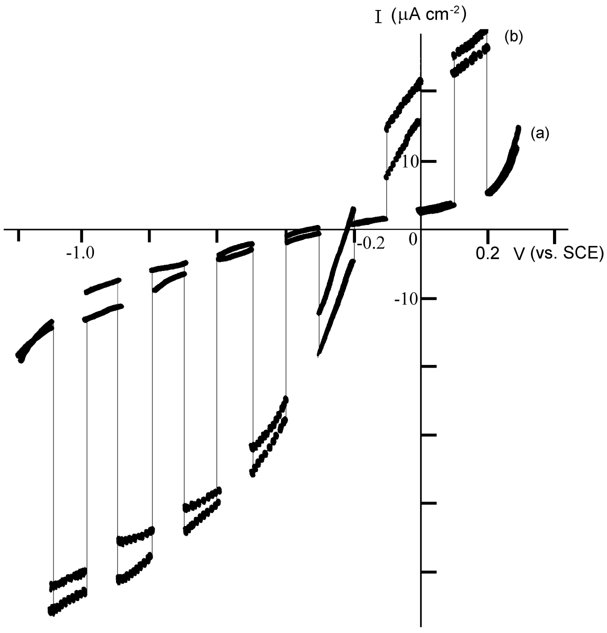

Figure 1: Current-voltage characteristic of layers of ZnS:Mn^{2+} nanocrystals dip-coated on a conducting substrate. (a) In the dark. (b) Under illumination with an excitation band of 250 to 390 nm. Measurements are performed at room temperature.

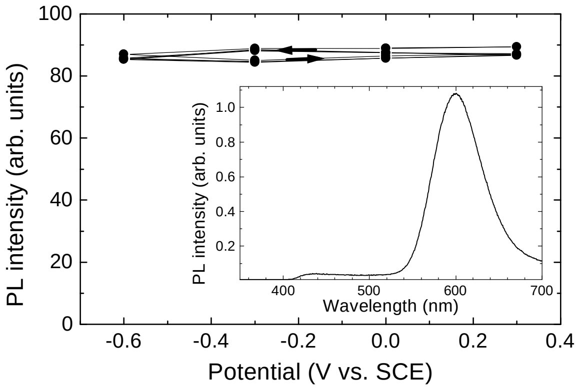

Figure 2: Potential dependence of the Mn^{2+} related photoluminescence of the ZnS:Mn^{2+} nanocrystalline electrode. Inset: a luminescence spectrum at V=0. Excitation was using a broad band of 250 – 390.

[1] L. Brus, *Pergamon* **59**, 459 (1998) and the references therein.

[2] J. F. Suyver, S. F. Wuister, J. J. Kelly and A. Meijerink. Nano Letters **1**, 429 (2001).

[3] J. F. Suyver, R. Bakker, A. Meijerink and J. J. Kelly. *Phys. Stat. Sol. B* **224**, 307 (2001).