Nanoparticle-Enhanced Chemiluminescence in Micro-Flow Injection Analysis

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Chemiluminescence (CL) detection for biomedical analysis has the principal advantage that no optical source is required so that instrumentation is simple and background radiation is minimised, resulting in high sensitivity. CL has been exploited in a wide range of chemical and biochemical measurements such as enzyme-linked immunoassays (ELISA), DNA sequencing, and for the analysis of biomedical, food and environmental samples [1]. CL is ideally suited to microfluidic flow-injection analysis (μFIA), due to the precise temporal and space control of sample/reagent aliquots [2]. However, while CL is a sensitive technique, the ultrasmall volumes employed in μFIA lead to low emitted power, so that signal enhancement methods are required to achieve suitable detection limits. Gold and silver nanoparticles (GNPs and SNPs) may provide enhancement of optical signals due to collective oscillation of conduction electrons excited by the electromagnetic field or due to catalysis [3,4]. In this study, CL of luminol was investigated in a microflow chip with a serpentine channel of width 600 μm, depth 75 μm and length 150 mm formed in polydimethylsiloxane (PDMS) by moulding over a 3D printed master. Dilute NaOCl was injected into one port of the flow system and dilute luminol and NaOH into the other (Fig 1a); light emission was recorded temporally and spatially using a CCD camera as shown in Fig. 1b. The procedure was repeated with the inclusion of GNPs and SNPs of various diameters, with only 60nm diameter SNPs described here for clarity.

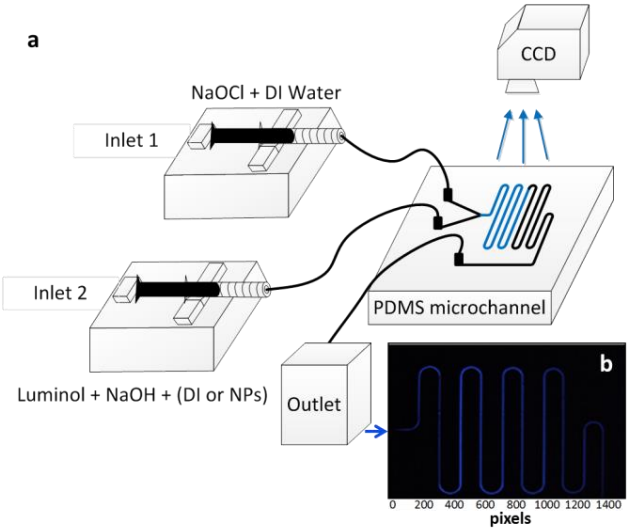

Fig. 1. (a) Schematic of the microfluidic device with syringes that pump the fluids through a chip whilst the emitted CL is measured. (b) Image of the light emitted with SNPs of 60nm diameter.

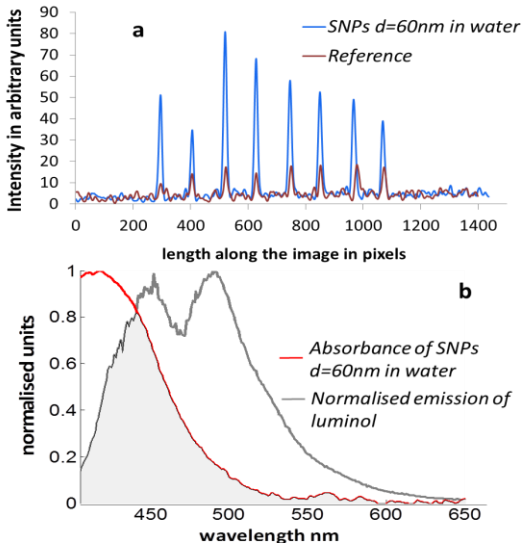

Fig. 2. (a) Intensity over a cross-section of the CCD images with and without SNPs. (b) Overlap between SNPs absorbance in water and emission of luminol.

Fig. 2a shows a section of the intensity distribution recorded on the CCD with and without SNPs of 60nm diameter, showing a average 3.5-fold enhancement of emitted CL light due to the addition of the SNPs. The enhancement mechanism can be explained by a combination of (i) excitation of localized SPs [3] and (ii) catalysis [4]. Fig. 2b shows the overlap of the resonant absorbance bands of 60nm SNPs in water with the emission spectrum of luminol, showing that the emission is at an appropriate wavelength to be enhanced. However, the plasmonic enhancement is short range and therefore the fraction of the liquid within the nanoparticle evanescent field is small resulting, in combination with nanoparticle-catalysed oxidation of luminol, in this small enhancement factor. The approach demonstrated in this paper has the potential to improve detection limits in many chemiluminescence assay systems.

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