Tip-selective functionalization of gold nanorods with dye-labeled DNA's for effective fluorescence enhancements

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Metal nanoparticles can act as optical antennas, coupling light more efficiently in the excitation and emission from fluorophores [1]. Their antenna effect has been explored for the development of plasmon-enhanced fluorescence biosensors, in which molecular recognition events are detected by fluorescence signals with intensified response [2]. In non-spherical particles, large fluorescence enhancements are obtained in surface regions where large near fields, or plasmon hot-spots, occur. Typically, these hot-spots are located in regions of large curvature, e.g. at the tips of gold nanorods (Figure 1A). In this contribution, colloidal gold nanorods were functionalized with dye-labeled oligos to optimize antenna effects for fluorescence signal enhancement. A tip-selective functionalization was implemented in order to specifically attach the fluorescent oligos at the plasmonic hot-spots. This approach afforded fluorescent dye-particle assemblies with a 15-fold increase in steady-state emission relatively to the same dye in the absence of the nanorod antenna (Figure 1B). As comparison, a non-selective functionalization of the gold nanorods produced highly loaded dye-particles, but without an effective fluorescence enhancement (Figure 1C). Dye-particle conjugates were further characterized by confocal fluorescence lifetime microscopy with single-particle sensitivity. The results reported here highlight the importance of site-selective approaches for hot-spot functionalization, maximizing plasmonic effects for applications in imaging or biosensing [3]. The gold nanoantennas developed have potential for nucleic acid detection using DNA-based receptors, since improved responses would allow achieving lower detection limits and increased sensitivity.

References

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Figures

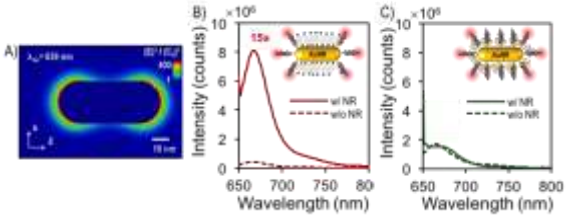

Figure 1 – A) Plasmon-enhanced near field map calculated for a gold nanorod (60 nm x 25 nm) excited at 639 nm. B and C) Fluorescence spectrum of dye-labeled oligos on gold nanorods (filled lines) and without nanorods (dashed lines) in aqueous solution excited at 640 nm. In the tip-selective functionalization, a fluorescence enhancement of 15-fold increase of emission was observed (B), while in the non-selective functionalization it is not observed enhancement (C).