Star-Shaped Gold Nanoparticles as Friendly Interfaces for Protein Electrochemistry: the Case Study of Cytochrome *c*

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Star-shaped gold nanoparticles (AuNSs) with an average tip-to-tip length of 52±6 nm have been employed as protein direct electron transfer (DET) promoters. To the best of our knowledge, this is the first time that non-spherical metal nanoparticles were used for this purpose. Specifically, DET of cytochrome *c* (cyt *c*) in solution was improved at AuNSs interfaces compared with gold nanospheres (AuNSphs) based electrodes. Therefore, the cyt *c* DET was evaluated in other two conditions: i) cyt *c* physically adsorbed onto AuNSs-modified pyrolytic graphite (PG) electrodes; ii) cyt *c*-AuNSs bioconjugates adsorbed onto pyrolytic graphite electrodes. The physical adsorption of cyt *c* onto AuNSs-PG electrodes induced the formation of a non-native species with peroxidase activity, wich was enhanced in presence of AuNSs. This platform (LOD=0,49 μM, linear range 1-20 μM) proved to be suitable for further improvements in order to realize a DET-based biosensor for H_2O_2 detection. Interestingly, the adsorption of cyt *c*-AuNSs bioconjugates onto PG electrodes shows the ritention of the protein native properties, proving that AuNSs represent a favourable microenvironment for the cyt *c*.

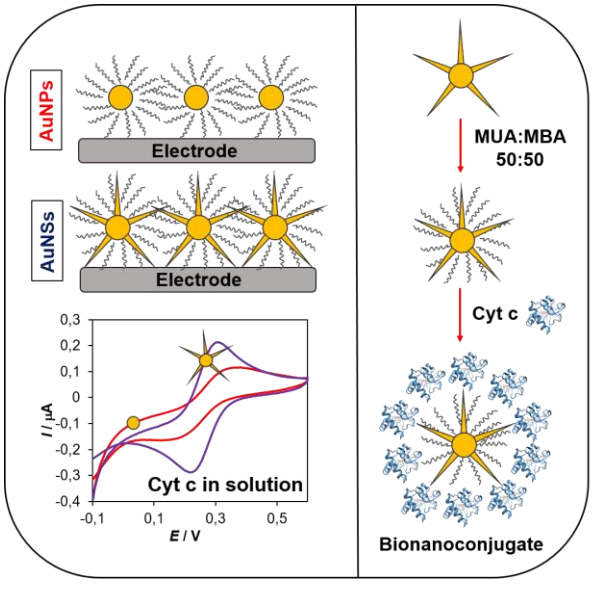

Figure 1. Schematic representation of cyt *c* DET enhancement promoted by AuNSs – PG interfaces (on the left) and bionanoconjugates formation via electrostatic interactions between cyt *c* (positive net charge at pH < pI=10) and negative charged capping agents.