INTERACTION OF FUNCTIONALIZED GOLD NANOPARTICLES WITH METAL IONS AND AMINE COMPOUNDS: DEVELOPMENT OF SELECTIVE ANALYTICAL METHODS.

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Gold nanoparticles have attracted a great deal of attention due to their size dependent physical and chemical characteristics. As a result, a variety of optical methods for different analytes using gold nanoparticles have been developed for sensitive determinations, such as colorimetric detection [1], surface plasmon resonance analysis [2], fluoresence [3-5] and scattering-based sensing [6]. This presentation deals with the interaction of functionalized gold nanoparticles with metal ions in order to tailor their optical properties for selective recognition of amine compounds. The model metal ions selected in this study were Eu^{3+} and Cu^{2+} and two model amine compounds were also considered: lysine (amino acid) and histamine (biogenic amine).

Recent experiments on the resonance light scattering properties of Eu^{3+} in gold colloid were made by A.Jian et al [7]. These authors reported the effects of gold nanoparticles on the fluorescence and resonance light scattering properties of europium ions and suggested an efficient energy transfer from the nanoparticles surface plasmon resonance to the metal ions. In this presentation, we report on the fundamental aspects of the role of europium ions on the resonance light scattering (RLS) properties of gold nanoparticles in solution phase. Our proposal is conceptually different from the above mentioned study as ours relies on gold nanoparticles functionalized with 11-mercaptoundecanoic acid (MUA) and the cooperative binding of europium ions and lysine to enhance the RLS properties of MUA-functionalized gold nanoparticles (Figure 1). Results demonstrated that upon addition of lysine to the MUA-GNPs-Eu(III) system, a hyper-Rayleigh scattering emission was observed, thus providing an inherently sensitive method for lysine determination. Finally, the analytical potential of the system and the mechanism for RLS enhancement is outlined.

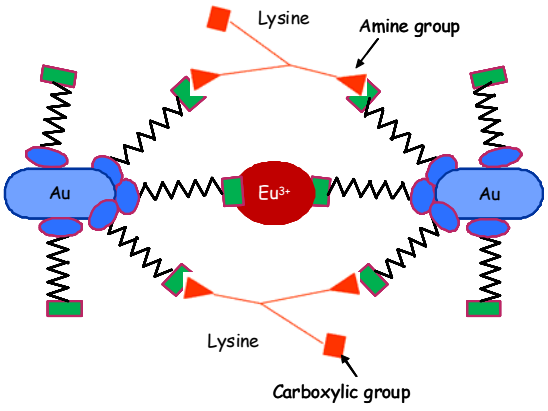

Figure 1. Schematic for MUA-GNPs resonance light scattering plasmon enhancement model through cooperative binding with europium and lysine [8]

On the other hand, addition of Cu^{2+} ions to the Au-MUA resulted in a red-shift in the absorption spectrum of gold-nanoparticles. The spectral changes observed may be explained on the basis of interplasmon coupling phenomena [9], suggesting that upon addition of the metal ions nanoparticles were brought into proximity. On the other hand, experimental data demonstrated that addition of histamine to the MUA-GNPs-Cu^{2+} system resulted in an enhanced absorbance at 600 nm of the histamine-Cu^{2+} complex. Other structurally related amines (cadaverine, putrescine, tyramine) commonly found in foods were assayed for selectivity and the system was applied to real sample food analysis (the content of biogenic amines may be indicator for freshness of fish raw material and thereby serve as a quality criterion for fish meal).

In conclusion: although differentiation between similar analytes is hard to achieve, small differences in chemical structure may make important differences in chemical action. In the systems described here metal ions and amine-compounds binding interactions, working in cooperation and coupled to gold nanoparticles, allowed for the amine-compounds discrimination from other structurally related through the enhanced RLS of gold nanoparticles and/or enhanced absorption.

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