Biocompatible Gold Nanoclusters as "Turn-off" Biosensors

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Noble metal nanoparticles vs. nanoclusters

The well-known biomolecules (eg. peptide, amino acid, nucleotide, etc.) are suitable for both direct preparation and stabilization of plasmonic Au NPs but the weight or molar ratios of the reactants have dominant role on the size and the optical feature. In addition to Au NPs, the fluorescent Au NCs can also be fabricated using this process. The Au NCs can be classified in the sub-nanometer range due to the application of large excess of biomolecules synthesis. which prevents association of the locally reduced metal seeds by steric stabilization. These ultra-small Au NCs show unique physical and chemical properties such as well-defined molecular structure. discrete electronic transitions or characteristic strong fluorescence. Both the NPs and the NCs are widely used biosensors because any change in the chemical environment causes measurable deviations in their optical properties. The sensor application of the Au NCs is usually based on the quenching or enhancing of their fluorescence.

Nucleotide-stabilized blue-emitting Au nanoclusters [1]

The one-step syntheses of both adenosine monophosphate (AMP) nucleotide-stabilized plasmonic gold nanoparticles (AMP-Au NPs) and fluorescent gold nanoclusters (AMP-Au NCs) were demonstrated. The dominant role of AMP:AuCl₄⁻ molar ratios on the formation of diverse Au products was the first time proven. Based on the results of numerous spectroscopic, HRTEM and DLS techniques the size, the structure and the unique optical

features of the nanoproducts were determined. The ultra-small AMP-Au NCs having blue fluorescence (λ_{em} = 480 nm) and were utilized to develop a selective sensor for detecting Fe³⁺ ions in aqueous medium based on fluorescence quenching. The defined limit of detection (LOD) was 2 μM and the dynamic range was appointed between 10-100 µM. The Stern-Volmer constants (K_{SV}) and various thermodynamic parameters (ΔG , ΔH° , ΔS°) of the quenching were determined by Stern-Volmer fitting of the fluorescence data. The quenching mechanism has been identified based these parameters.

Immunoglobulin-stabilized red-emitting Au nanoclusters

The proteins are the well-known reducing and stabilizing agents during the "green" synthesis methods [2]. The production of plasmonic and fluorescent gold-base nanohybrid systems was successful by using the γ-globulin as reducing and stabilizing agent. The several nm sized yG-Au NCs exhibit red emission at 645 nm and show high kinetic stability at physiological conditions. Thus, they may be suitable for selective detection of L-kynurenine (Kyn), which is the first intermediate of the physiologically important kynurenine pathway. The detection limit (LOD) of 15 µM and the dynamic range of 15-100 µM were obtained. Beyond the definition of the analytical parameters (K_{SV}, k₀, k_q) the nature as well as the proposed mechanism of the quenching process was also suggested based on the determinative thermodynamic parameters (ΔG , ΔH° , ΔS°) of the interaction.

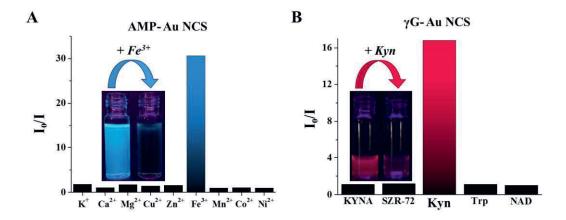


Fig. 2. The relative fluorescence of the (A) adenosine monophosphate-stabilized and the (B) γ-globulin immunoprotein-stabilized Au nanoclusters with the presence of the studied ions and biomolecules.

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References

- [1] D. Ungor, E. Csapó, B. Kismárton, Á. Juhász, I. Dékány, Nucleotide-directed syntheses of gold nanohibrid systems with structure-dependent optical features: Selective fluorescence sensing of Fe³⁺ ions, *Colloids and Surfaces B: Biointerfaces* 155, 135-144 (2017), doi: 10.1016/j.colsurfb.2017.04.013
- [2] V. Hornok, E. Csapó, N. Varga, D. Ungor, D. Sebők, L. Janovák, G. Laczkó, I. Dékány, Controlled syntheses and structural characterization of plasmonic and red-emitting gold/lysozyme nanohybrid dispersions, Colloid and polymer science 294, 49-58 (2016), doi: 10,1007/s00396-0,15-3781-7