

Biomolecule Stabilized Gold Quantum Clusters – Preparative Aspects, Characteristics and Behavior of Products

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Statements of the thesis

1

I have prepared a novel photoluminescent material by reacting tetrachloroaurate with L-cysteine. In the range between room temperature and 75 °C, I have observed the formation of an orange-emitting nanomaterial with a layered structure. The periodic distance between the layers was 1.3 nm, the average thickness of the particles was 8 nm. After mixing the precursors, the formation of a yellow non-luminescent precipitate can be observed, which spontaneously transforms into the photoluminescent product. The formation of the layered structure correlates with the appearance of the photoluminescence. It has been evidenced that layers are held together by aurophilic bonds, the cohesion is supported by hydrogen and ionic bonds between the functional groups of L-cysteine molecules. The stoichiometry of Au and L-cysteine in the product is 1:1. Gold is in an oxidation state between 0 and +1. Results have shown that the properties of the new product are different from those of Au-L-glutathione species.

2

The formation of photoluminescent gold clusters has been investigated using photoluminescence spectroscopy. Based on experiments using proteins (hyaluronidase-3, bovine serum albumin, trypsin, concanavalin A), peptides, and amino acid mixtures, it has been concluded that the necessary and sufficient condition for cluster formation is the presence of cysteine and tyrosine residues in the polypeptide backbone. The amino acid sequence of the biomolecules does not play an important role in cluster formation. Cysteine residues can be effective as free thiols and also as disulfides. Cysteine cannot be replaced with methionine, and tyrosine cannot be replaced with tryptophan. Experiments using amino acid mixtures containing free L-cysteine and L-tyrosine did not result in the formation of gold quantum clusters.

3

I have concluded that the molar ratio of precursors is a crucial factor in cluster formation. A critical protein:gold (or peptide:gold) ratio has been defined, referred as ϕ_c , above which gold clusters form. Based on literature data and experimental results, the value of ϕ_c is inversely proportional to the number of cysteine residues in a single biomolecule. The reaction of tetrachloroaurate and

biomolecules with the potential to make clusters leads to cluster formation in case the protein:gold (or peptide:gold) ratio is not less than ϕ_c . If it is less than ϕ_c , nanoparticles form. Based on simulations using molecular mechanics and Fourier-transform infrared spectroscopy, it has been shown that the formation of photoluminescent products correlates with conformation changes in the biomolecules.

4

Photoluminescent gold clusters stabilized by bovine serum albumin have been embedded in an aqueous phospholipid multilamellar system. The presence of clusters has been evidenced via monitoring structural changes, and also via direct visual information obtained by electron microscopy. Clusters have been anchored to the lipid layers by Ca^{2+} ions. Photoluminescence of gold clusters was detectable after intercalation, the emission wavelength of the embedded clusters showed a blue shift compared to that of the native cluster-protein conjugates.

5

It has been pointed out that the intercalation of BSA protected gold clusters results in significant changes in the thermotropic properties of the aqueous lipid system, a new nano-superstructure forms with a high level of interlayer correlation. Emission properties of the embedded clusters show temperature dependence in a range close to the temperature of the human body. The emission wavelength varies with changing temperature due to the complex interactions between cluster-protein conjugates and the lipid double layers. The emission intensity show temperature dependence due to conformational changes of the protein.