

Thesis:

Gold Nanoparticle-Chromophore Systems: Assembly and Photophysical Interactions

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Abstract

Gold nanoparticle-chromophore systems were prepared using two assembly strategies: thin films and functionalization of the metal cores with chromophores. These assemblies were studied with steady-state and time-resolved spectroscopic techniques and the thin films also with photoelectrical and microscopic methods.

Controlled assembly of gold nanoparticles and chromophores into solid structures is necessary for building photoactive devices but the design of applications relies on knowledge of photoinduced processes within the gold nanoparticle-chromophore systems. Alternating thin films of gold nanoparticles and chromophores were prepared using Langmuir-Blodgett and – Schäfer techniques. The photoelectrical measurements indicate that the particles can function either as electron acceptors or donors to the photoexcited chromophores, demonstrating the active role of the gold cores in photoinduced charge transfer reactions in films. Photoinduced electron transfer takes place from a poly(hexylthiophene) layer to an adjacent gold nanoparticle layer, and in the case of a porphyrin or a fullerene layer, the gold nanoparticles donate electrons to these chromophores. While photoelectrical measurements demonstrated charge transfer in the films of porphyrins and gold nanoparticles, also energy transfer was considered to be possible. Time-resolved spectroscopic measurements showed that most, more than 80%, of the photoexcited porphyrins decay by energy transfer to the gold nanoparticles, whereas charge transfer is a minor relaxation route. Both energy and charge transfer processes are known to take place in chromophore-gold nanoparticle systems and in the case of porphyrin-gold nanoparticle films the relative importances of these two processes could be estimated.

The highest photoelectrical signal was observed for films combining gold nanoparticles and porphyrin-fullerene dyads. Films of porphyrin-fullerene dyads and gold nanoparticles are a step towards the construction of both structurally and functionally more complex systems. Porphyrin-fullerene dyads are known to undergo intramolecular photoinduced charge transfer via an exciplex intermediate state. Certain type of porphyrin-fullerene dyads can organize in Langmuir films, and thus the porphyrin moieties of the dyad are located on their own plane adjacent to the plane formed by the fullerene moieties. A gold nanoparticle layer enhances charge transfer of the dyad significantly, when placed near the porphyrin moieties of the dyads. In addition, fluorescence measurements indicated that the adjacent gold nanoparticle layer affects the relaxation of the exciplex state of the dyad.

The thin film strategy followed was successful in organizing the particles and chromophores at close distances. The way to control even better their organization is to attach the chromophores directly to the metal core surface. Porphyrin- and phthalocyanine-functionalized gold nanoparticles were prepared using a ligand exchange method. Photoexcited porphyrins transfer energy very rapidly, in few picoseconds, to the gold cores as shown by time-resolved fluorescence measurements. The packing of the porphyrins on the gold nanoparticle surface and their fluorescence lifetimes are dependent on position of the linkers on the porphyrin molecule.

The phthalocyanine-functionalized gold nanoparticles offered a possibility to study the photoinduced processes in more detail because both of the components could be excited nearly selectively. Time-resolved absorption measurements were used to study their fast photoinduced processes. Selective excitation of the phthalocyanines leads also to electron transfer to the gold cores, and most likely also to energy transfer. The role of gold cores as energy acceptors in chromophore-functionalized gold nanoparticles has been widely studied and reported, whereas observations of gold cores acting as electron acceptors are few. Selective excitation of the gold cores in phthalocyanine-functionalized particles results in energy transfer to the phthalocyanines, demonstrating that the gold cores can behave as energy donors.

These results show that although the photoinduced processes of gold nanoparticle-chromophore systems are generally known, they are strongly affected by the choice of the chromophore and by the design of the system. The next step in assembling chromophores and gold nanoparticles would be to organize functionalized gold nanoparticles into solid structures. These systems offer many possibilities for controlling organization and thus the rates of photoinduced processes. Tunable parameters could include, for example, size and choice of the metal nanoparticle, choice of the chromophores, orientation and distance of the chromophore relative to the metal core and excitation energy. The gold nanoparticle-chromophore systems are a fragment of the booming area of nanotechnology that is and continues to develop, more and more as a part of everyday life and not just something from the pages of science fiction books.