ASSEMBLY OF GOLD AND MAGNETIC NANOPARTICLES BY AMINO ACIDS, PROTEINS, AND DNAS

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The exploration of nanotechnology in medicine and biology has played an increasingly-significant role in controlled drug delivery, medical diagnostics and biosensing. This presentation discusses recent findings of our investigations of the assembly of gold (Au) and magnetic nanoparticles (5-60 nm) to probe the biointerfacial reactivities in three systems, including amino acids (e.g., homocysteine, cysteine and glutathionine), proteins, (e.g., antibody/antigen), and DNAs.

One example for amino acids involves probing the interfacial interactions of Au nanoparticles with homocysteine (Hcys), a thiol-containing amino acid. Research has shown that a concentration of >15 μM Hcys in blood (hyperhomocysteinemia) is often considered an indication of cardiovascular disease, and is linked to Alzheimer's disease, pregnancy complications, and osteoporosis. Current analytical techniques for determining the Hcys concentration are time-consuming and are often complicated by the need of chromophore labeling. The monitoring of the unique surface plasmon resonance absorption of Au nanoparticles in the presence of Hcys allowed us to address two fundamental issues [1], including the reaction kinetics and the assembly-disassembly processes (Scheme 1). The findings of the fine tunability on the non-covalent and electrostatic interparticle interactions constitute the basis for the development of colorimetric nanoprobes for amino acids.

For proteins, one example is the detection of specific antibody/antigen (Ab/Ag) binding via covalent linkages of the Ab/Ag onto the surface of Au and Au-coated magnetic nanoparticles (e.g., Fe_3O_4@Au) [2]. Upon assembly between Ab-capped-Au coated magnetic nanoparticles and Ag-capped Au nanoparticles labeled with a Raman active probe (e g., Mercaptobenzoic acid-MBA), a magnetic field was applied to collect the Ab-Ag-binding products for surface-enhanced Raman Spectroscopy (SERS) analysis (Scheme 2, left). The expected SERS signatures of MBA were detected at 1081 and 1591 cm^{-1}, corresponding to the ν(CC) ring-breathing modes of MBA (Scheme 2, right). The immobilization of biological recognition sites on Au-coated magnetic nanoparticles and the subsequent recognition to the targeted proteins provide an effective means for the separation of biological molecules.

An example for the DNA system explores a new strategy for manipulating the assembly/disassembly processes of DNA-Au nanoparticles by molecular intervention [3]. Using the temperature-induced assembly and disassembly processes of DNAs and Au nanoparticles as a model system, the introduction of a molecular recognition probe (P1) is demonstrated to lead to the intervention of the assembly/disassembly processes depending on its specific biorecognition (Scheme 3, left). This process can be monitored by changes in the optical properties of Au nanoparticles and their DNA assemblies (Scheme 3, right). The formation of the P1-DNA recognition product (P2) provides opportunities for further tuning and intervening the interfacial reactivities in the DNA-nanoparticle system.

The findings of these investigations have provided new insights into the precise control of interfacial interactions and reactivities between the biological molecules immobilized on specifically-tailored nanoparticles, and have broad implications to the development of biorecognition-based assays, drug targeting/delivery, and biomaterials engineering.

Acknowledgement: *This work is supported by the National Science Foundation Stephanie Lim acknowledges the support of the NSF Graduate Research Fellowship. Discussion and help from Hye-Young Park, Lingyan Wang, Uma Chandrachud and Dr. Susannah Gal are also acknowledged.*

References:
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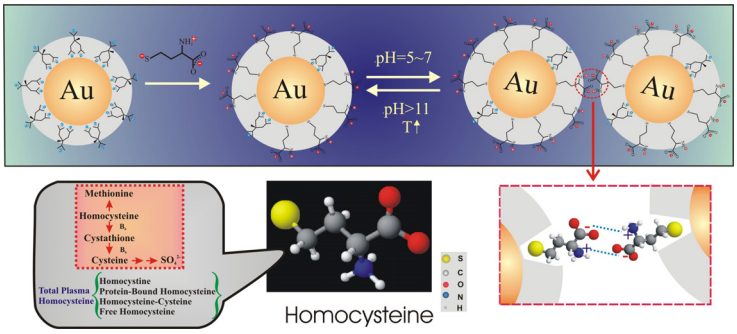
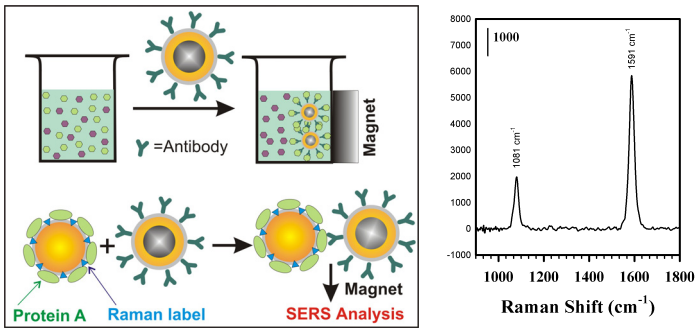
Schemes:

Scheme 1: A schematic diagram of the electrostatic interparticle interactions in the assembly/ disassembly of homocysteine-capped Au nanoparticles.



Scheme 2: (Left) Illustrations of the separation of antibody-labeled Fe_3O_4@Au nanoparticles in reaction with protein A capped Au nanoparticles which are labeled with MBA. (Right) SERS spectra of the products separated magnetically form the reaction.



Scheme 3: (Left) A schematic diagram (not to scale) illustrating: (S1) the assembly and disassembly of DNA1-capped Au (A1) and DNA2-capped Au (A2) nanoparticles via a target DNA (T1) upon changing the temperature (▲= heat; ▼= cool); and (S2) an intervention of the disassembly by the introduction of P1 into the heated solution which leads to the formation of P2 upon returning to room temperature. (Right) Spectral evolution of the SP band showing the reactivity upon heating and cooling of solution-S1 in the presence of an uncleaved DNA (P1).