Self-Assembled Gold Nanoparticles for Biosensing Applications

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Introduction:

Localized surface plasmon resonance (LSPR) is a collective oscillation of conductive electrons of metal nanoparticles, produced by light excitation under certain conditions [1]. The LSPR wavelength at which the resonance occurs is extremely sensitive to changes in the refractive index and, consequently, to the composition of the nanoparticle environment. The LSPR wavelength shift can then be measured and used to detect molecules adsorbed on the surface of the nanoparticle, which is known as LSPR spectroscopy [2]. The assembly of these nanoparticles generates a plasmonic coupling between adjacent particles, leading to significant sensitivity enhancement [3]. Such a property makes nanoparticle assemblies an attractive platform for biosensing applications. However, the use of these assemblies for biosensing applications requires the generation of stable nanoparticle clusters along with their efficient transfer to solid substrates.

This study presents a controlled, rapid process for self-assembly of gold nanoparticles (AuNPs) using aminothiols and a method to transfer AuNP assemblies onto substrates, while preserving the assembly structure and optical properties. AuNPs were self-assembled using p-aminothiophenol (pATP) as a crosslinker. The assemblies were then transferred to glass and silicon substrates by immersion and examined using ultraviolet-visible spectroscopy (UV-Vis), Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

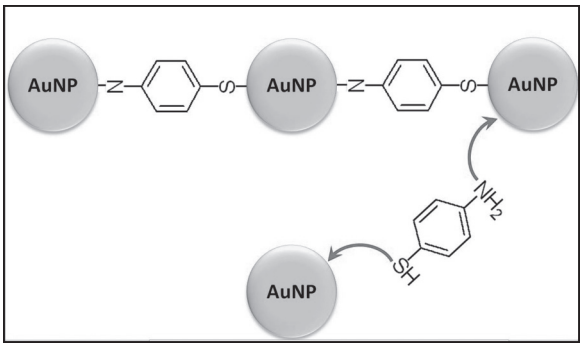

Figure 1: The mechanism for self-assembly of AuNP with pATP.

Experimental Procedures:

AuNPs were synthesized using the standard method of reducing chlorauric acid with sodium citrate [4]. For self-assembly, the AuNP solution was diluted to a desired concentration, and pATP was added. As shown in Figure 1, the mechanism for self-assembly involves the amino group on one end of the pATP molecule binding with a AuNP, and the thiol group on the other end binding with another AuNP. By varying the concentrations of pATP, the self-assembly could be "frozen" at different stages, ranging from dimers to branched networks. The distinct optical properties of the solutions resulting from different concentrations of PATP are shown in Figure 2.

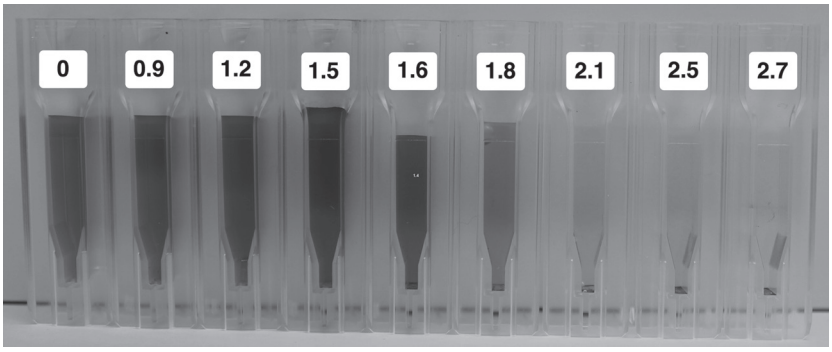

Figure 2: AuNP assemblies with increasing pATP concentrations from left to right.

To enable the transfer of AuNP assemblies onto solid substrates, glass and silicon substrates were functionalized using two different methods: polyelectrolyte multilayers (comprised of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS)) using

layer by layer (LbL) assembly or a single layer of 3-aminopropyltriethoxysilane (APTES). A spin coater was used to deposit 3.5 bilayers, ending on PAH, on substrates for the LbL method. For the APTES method, substrates were immersed in APTES solution for 20 minutes and sonicated in water for one hour. The negatively charged citrate-capped AuNPs adsorbed to the positively charged top layer of PAH or APTES through electrostatic interactions.

The self-assembled AuNPs were deposited onto the substrates by immersing the substrates in the assembled AuNP solution. LBL substrates were immersed for 2 h and 40 min, while APTES substrates were immersed for three days. After immersion, the substrates were rinsed and stored in water.

Results:

Figure 3 shows the UV-Vis extinction spectra of AuNP solution without and with assembly, demonstrating a clear change in AuNP optical properties with the addition of pATP, evidenced by the appearance of a second peak. Extinction spectra of the glass substrates immersed in these solutions, also shown in Figure 3, exhibited peaks at the same wavelengths and with the same shapes, but with lower relative intensities, indicating the successful deposition of AuNP assemblies onto the substrates while retaining their properties as compared to the assemblies in solution.

Figure 4 depicts the results of AuNP transfer with varying pATP concentrations. The SEM images of AuNP assemblies clearly indicate an increase in the extent of assembly (i.e. individual particles to dimers to finally a network-like structure) with increasing pATP concentration.

Conclusions:

The use of pATP as a crosslinker for AuNP self-assembly is a very efficient and versatile technique. By varying the molar ratio of pATP/AuNP, the extent of AuNP self-assembly can be finely controlled. Furthermore, the immersion of APTES or polyelectrolyte functionalized solid substrates in AuNP solutions during the assembly process leads to the transfer of AuNP assemblies with a high degree of fidelity by retaining their structure and optical properties. The sensitivity and analytical parameters of assembled AuNP on solid substrates and their use for biological sensing are under investigation.

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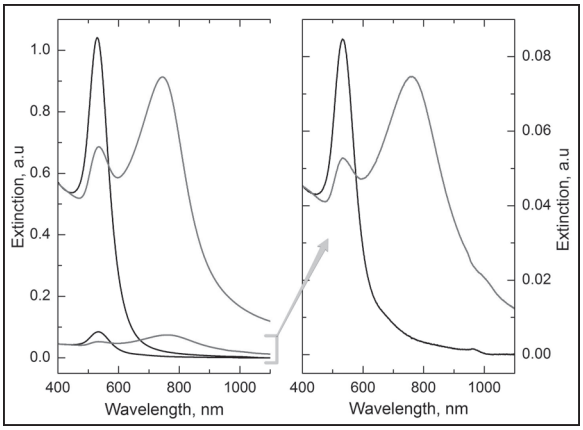

Figure 3: UV-visible extinction spectra of AuNP with (gray) and without (black) assembly. Left: Spectra for AuNP in solution and on substrates, with AuNP in solution having a higher relative intensity. Right: Spectra of AuNP on substrates.

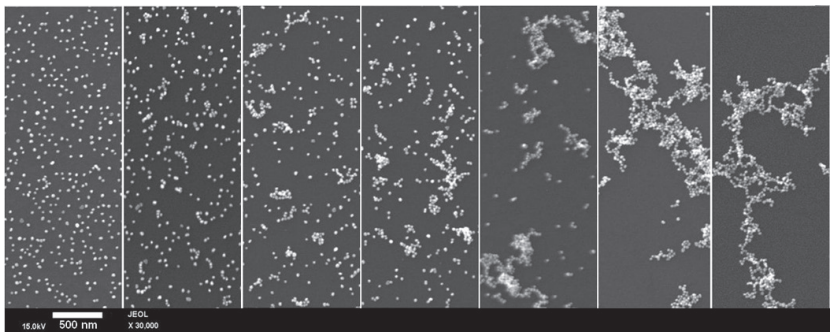

Figure 4: SEM images of assembled AuNP on silicon substrates with increasing pATP concentration from left to right.