

Gold Nanoparticles for Stimuli-Responsive Aggregate Assembly

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Colloidal gold has been in use for making glass and decorating ceramics since the 5th - 4th B.C.¹, yet documented scientific study did not formally surge until the nineteenth century when Michael Faraday first reported on the optical properties of these solutions.² Since then, scientific interest resurged by the late 20th century in terms of synthetic routes, stabilization, catalysis and sensing.¹ In recent years, there has been a surge in exploring gold nanoparticles (AuNPs) for self-assembly. Various other materials have been studied for self-assembly; including polymeric colloid systems and other inorganic nanoparticles, but AuNPs offer several advantages as a model system.³ As a noble metal, AuNPs are highly chemically stable as compared to other inorganic nanoparticles that can be chemically reactive in a given environment. They are also well characterized for surface modifications, such as decorating with sulfur ligand monolayers⁴⁻⁵ that can be used to direct assembly. Another strong advantage is the plasmon resonance band (PRB) for AuNPs below 100 nm that absorbs c.a. 530 nm and redshifts with increasing particle diameter.^{1,6} This in turn can be easily used to track the size of nanoparticle assemblies by UV-Vis spectra.

Recently, there has been increasing interest in making reversible AuNP assemblies. Reversibility becomes important for these systems to be used effectively in technological applications. Therefore, stimuli-responsive assemblies have gained interest due to their ability of reversing assembly when the stimuli is employed or removed. Stimuli that have been gained attention for their simplicity include temperature, redox activity, pH and light. These systems in general make use of a stimuli-responsive material that can be incorporated into the AuNP system albeit as a surface modification using self-assembled monolayers (SAMs)⁴ or as an additive in the medium.

Early examples by the groups of Meskers and Schenning make use of temperature sensitive π - π stacking surface ligands on AuNPs to make highly spherical assemblies that form at room temperature, but can be disassembled at higher temperatures (Figure 1).⁷⁻⁸ AuNPs of metallic diameters of ~2 and 4 nm functionalized with oligo(*p*-phenylene vinylene) (OPV) formed highly stable micrometer-sized spherical aggregates at room temperature. The aggregates formed by non-covalent interactions were even stable enough to be manipulated by atomic force microscopy (AFM) when drop-casted onto a substrate, demonstrating possibilities to use these aggregates for nano-plasmonics.

Another system that has surged based on π - π stacking is that of redox stimulated pseudorotaxane⁹ formation by Klajn and coworkers. In this case, an oxidizable tetrathiafulvalene ligand is used to decorate the AuNPs, which in its neutral state forms a pseudorotaxane with a polymer in solution (Figure 2). The aggregates formed by the threading of the tetrathiafulvalene ligands into the polymer's macrocyclic substituents are easily reversed by either chemical or electrochemical means.¹⁰ This gives the system versatility

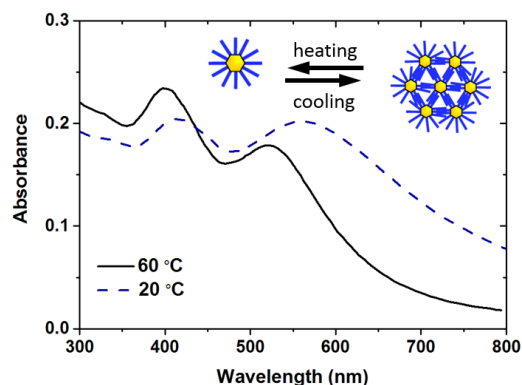


Figure 1. UV-Vis spectra of temperature dependent behavior of OPV functionalized AuNPs suspended in n-butanol. The PRB peak shifts at lower temperatures. (Adapted from 8)

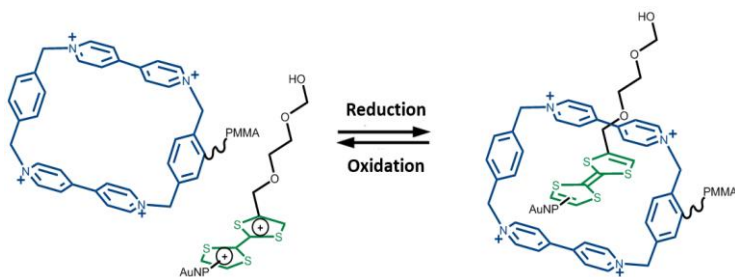


Figure 2. Pseudorotaxane behavior triggered by oxidation state of thiol ligand on AuNP. (Adapted from 10)

for switchable catalysis as the methodology could be transferred to different metal centers that are catalytically active and be turned off by the redox-switchable aggregation. Nevertheless, this would require that the nanoparticle core be inactive to redox processes. For instance, the authors tested this methodology with silver cores, which worked

reversibly by chemical redox, but electrochemical oxidation of silver would interfere with the ligand oxidation and decompose the particles.¹⁰ Therefore, this study showed the exemplary stability of gold nanoparticles as compared to other systems.

The stimuli that has received the most attention for AuNP reversible self-assembly has been that of light. Examples range from using light sensitive ligands assembled on the AuNP shell¹¹⁻¹² to having the responsive molecules added into solution¹³ rather than being part of the particle itself. Classic photoswitchable molecules such as azobenzenes and spiropyrans have been used in these systems. Azobenzenes undergo isomerization between cis and trans forms which forms a dipole in the cis form that can interact with neighboring azobenzene units.¹⁴ Meanwhile, spiropyrans undergo a reversible C-O bond cleavage when illuminated with UV light.¹⁵ The Grzybowski group demonstrated the importance of azobenzene ligand loading on reversibility of light triggered AuNP assemblies in 2007. They showed that the dipole-dipole interactions between azobenzene functionalities on the ligands was not enough to assemble ordered structures. Instead, the assemblies required crosslinking the nanoparticles using thiols at both ends of the ligand. Nevertheless, reversibility of the process was suppressed at high ligand coverage of the AuNPs.¹²

Thus, attention has been given mostly to spiropyran systems for reversibility. There have been many studies where the AuNPs are decorated with monolayers of spiropyran ligands that can be triggered to assemble upon UV irradiation.³ One such study utilizes monolayers of mixed spiropyran decorated vinyl polymers and polyethylene brushes grafted from the gold surface to tune the size of aggregates formed dictated by the ratio of polyethylene to spiropyran.¹¹ These small aggregates showed promise to be used as signal enhancers in Raman scattering applications.

Recent directions using spiropyran triggers are moving away from the monolayer method to simply adding the trigger into the media. In a very recent study in the Klajn group, carboxylic acid terminated ligands were used on AuNPs in an acidic medium containing spiropyran. The acid present in solution would maintain the AuNPs dispersed when irradiated with blue light. When the light was turned off, the AuNPs would aggregate due to the spiropyran undergoing C-O cleavage and forming protonated merocyanine (Figure 3a). To capture the utility of this method, the AuNPs were confined into a polyethylene glycol gel where they could be used as inks (Figure 3b).¹³ Although this method shows promise for use in disappearing inks, to make the AuNP responsive it still has to be decorated with pH sensitive ligands. Thus, it is a novel way of stimulating assembly, but it still requires monolayer functionalization in addition to the modification of the media.

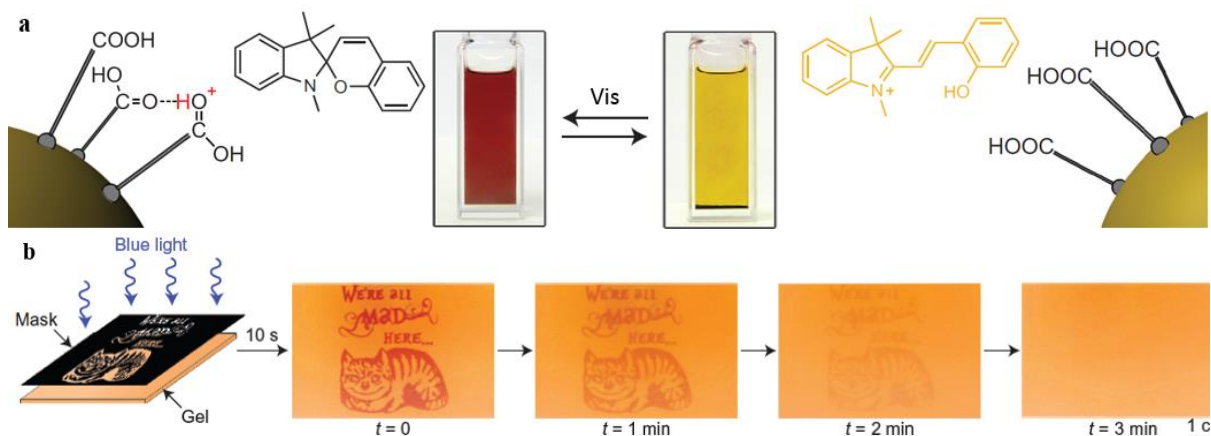


Figure 3. (a) When irradiated with UV, spiropyran forms and AuNPs disperse by hydrogen bond formation in the acidic medium. (b) Possible use of self-assembling AuNPs as a disappearing ink in PEG gel.¹³

In sum, in the last two decades there have been many advances in creating stimuli-responsive AuNP aggregates. Recent investigations are especially interested in reversible aggregates that can be tuned for size and/or shape depending on the possible application. Investigations into temperature, redox and light responses show high versatility in that the stimuli can be easily turned on and off as compared to other stimuli such as pH or solvent polarity which could involve changes in volume. The systems presented can be self-contained to respond to the external stimuli whether it is an electrode, radiation, or temperature. Future studies will likely demonstrate translations from the methodology used in AuNPs to other metal core systems.

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