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Spontaneous Self-Assembly and Disassembly of Colloidal Gold Nanoparticles Induced by Tetrakis(hydroxymethyl) Phosphonium Chloride

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Abstract

Upon reacting with tetrakis(hydroxymethyl) phosphonium chloride, 15 nm citrate gold nanoparticles rapidly assemble into linear chains, followed by slowly disassembling into monodisperse components. This work highlights the first example of ³¹P NMR on gold particles of this size and suggests that the phosphonium is oxidized on-particle, contributing to particle disassembly.

Graphical Abstract

The mechanism behind self-assembly and disassembly of gold colloids driven by addition of a phosphonium was characterized using ³¹P NMR.

The hallmark of nanotechnology lies in the responsibility of adsorbed nanoparticle capping ligands to prevent materials from returning to the bulk phase. Gold nanoparticles (AuNPs) in particular have been synthesized with thiol, amine, and phosphorus capping ligands in order to avoid aggregation.^[1] The structural features of ligands on small AuNPs (<5 nm) have been extensively characterized, which is made possible by the formation of dense

[†]Electronic Supplementary Information (ESI) available: Experimental methods, UV-vis spectra, ICP-OES results, ³¹P NMR, XPS spectra.

monolayers and the high concentration of adsorbed ligands that transduce spectroscopic signatures.^[2] However, the characterization of capping ligands on larger colloids is often performed empirically, rather than via direct spectroscopic methods due to the lower concentration of adsorbed ligands. In this investigation, we take advantage of empirical evidence provided by the optical properties of 15 nm AuNPs, followed by direct evidence from ³¹P nuclear magnetic resonance (NMR) to hypothesize a mechanism for self-assembly and subsequent disassembly of AuNP chains induced by a well-known tetrakis(hydroxymethyl) phosphonium chloride (THPC) capping ligand.

THPC has been extensively exploited as a strong reducing agent to synthesize aqueous 2–4 nm AuNPs under basic conditions.^[3] The rapid, reproducible synthesis of these small particles has afforded electroless plating strategies of microparticle platforms, as the THPC AuNPs serve as seed-mediated templates.^[4] However, to our knowledge, THPC has never been utilized to spontaneously assemble and disassemble colloidal suspensions of AuNPs. Previously, colloidal AuNPs have been shown to self-assemble into ordered one-dimensional and two-dimensional structures upon exposure to various stress-induced stimuli such as salt,^[5a] pressure,^[5b] temperature,^[5c,d] pH,^[5e] organic solvents,^[5a,f,g] DNA interactions,^[5h,i] and alkanethiol ligand exchange.^[5f,j,k] Many of these AuNPs employ phosphine capping ligands for stability due to strong, non-covalent interactions with the Au surface.^[5a–c] These noble metal particles form ordered linear assemblies similar to nanorods, transmitting tunable colors in solution that can be attributed to surface plasmon coupling.^[6] The reversible assembly and disassembly of nanomaterials without salt or physical forces poses a significant challenge because the electrostatic repulsion afforded by the surrounding media must overcome the van der Waals interactions from the adsorbed capping ligands and the inherent dipole moment of the particles.^[5c,k] However, in this work, we observe assembly only utilizing a THPC capping ligand, and AuNP disassembly is achieved without physical forces or external additives. Notably, the use of ³¹P NMR to understand THPC chemistry provides a means to further understand the role of phosphorus capping ligands in AuNP assembly and stability.

Upon incubating 15 nm citrate-stabilized AuNPs with 100 μ M THPC, the particles instantly undergo a red-to-blue color shift, which is reflective of the presence of an additional longitudinal SPR band at 680 nm in the UV-vis spectrum (Figure 1a). THPC can promote the rapid formation of linear assemblies in a similar manner to a short alkanethiol due to the rapid displacement of citrate ions.^[5f] After approximately five minutes, the longitudinal band begins to blueshift before ultimately disappearing, as the particles break apart into smaller assemblies over the next 48 hours (Figures 1b–d). The assembly of the particles into linear chains and subsequent disassembly into monodisperse spheres occurs spontaneously, requiring no additives, pH changes, or temperature variability. THPC remains adsorbed to the particles, as evident by quantitative ICP-OES and observations of particle stability after enduring multiple centrifugation cycles (Figures S2,S3). Additionally, excess citrate does not significantly displace the THPC on the particle surface, suggesting that THPC remains adsorbed to the surface throughout the assembly/disassembly process. Due to the high ionic strength of the solution, significantly less ligand is required to initiate the reaction relative to the rather high mM salt concentrations previously reported.

To investigate the mechanism of THPC AuNP disassembly, the particles are reacted with salt, acid, and base (Figure S4). These particles can be manipulated via acid/base chemistry to finely tune the SPR band and control the number of particles per chain. It is observed that the particles rapidly disassemble in the presence of NaOH, whereas the disassembly process is quenched in the presence of HCl. At four time intervals following THPC addition, 6.6 mM HCl is added to quench disassembly and the stability is monitored (Figure 2). The particles are stable for 24 hours after HCl addition, as indicated by the negligible change in UV-vis absorbance spectra over time. Thus, quenching the THPC disassembly reaction allows for precise manipulation of the size of the AuNP chains and the SPR band. We hypothesize that disassembly is initiated because the ligand undergoes a chemical change upon adsorption. Upon reacting THPC with NaOH in bulk solution, Hoffman first observed a THPC oxidation while Grayson elucidated the mechanism of conversion to tri(hydroxymethyl) phosphine oxide (THPO).^[7] Because this aqueous chemistry is well characterized, we hypothesize that this reaction can also proceed on-particle. It is plausible that an oxidized THPC ligand adsorbed to the nanoparticle surface cannot maintain the van der Waals interactions necessary for particle assembly.

As the pH of the citrate-stabilized AuNP suspension increases, the rate of THPC AuNP disassembly also increases (Figure S5). This rate of disassembly can be monitored by measuring the particle absorbance ratio ($A_{680\text{ nm}}/A_{520\text{ nm}}$) after THPC addition. The rate of decay follows an exponential trend relative to pH, which suggests pseudo second-order order kinetics similar to the THPC oxidation mechanism elucidated by Grayson in bulk solution (Figure S6).^[7c] The decay constant observed at pH 9.6 ($k = 0.15\text{ M}^{-1}\text{ min}^{-1}$) is consistent with that reported by Grayson ($k = 0.166\text{ M}^{-1}\text{ min}^{-1}$), although at a reduced pH value compared to Grayson's system (pH 13).

The assembly/disassembly process was further confirmed by using dynamic light scattering and zeta potential to measure the hydrodynamic diameter and surface charge of the particle aggregates. Upon addition of THPC the particles immediately aggregate to assemblies of about 170 nm in diameter and begin to disassemble after about five minutes, which correlates to the time that the UV-Vis spectra begin to blueshift (Figure S7). Following incubation with THPC, the zeta potential initially decreases to more negative values, followed by an increase to a final value of approximately -25 mV over a reaction period of two days (Figure S8). The initial decrease in zeta potential may be explained by the deviation from ideal conditions of monodispersity and the large size of the assembly, which slows the electrophoretic mobility of the particles, the property that is measured in order to calculate zeta potential.

In order to characterize the phosphorus species adsorbed to the particles, ^{31}P NMR spectroscopy is employed at different time intervals in the reaction. The ^{31}P NMR spectral profiles of THPC and its derivatives are well characterized in aqueous solutions.^[8] Our ^{31}P NMR spectral profiles of pure ligand in deionized water reveal multiple peaks, as the oxidation reaction progresses above the ligand's pK_a (5.5). However, under acidic conditions, a dominant THPC peak (δ , +26 ppm) and a smaller peak representing THPO (δ , +49 ppm) are elucidated, consistent with previous reports (Figure 3a). Upon adsorption to the particles, a dominant peak is observed at all time points after THPC addition (δ , +36

ppm) (Figure 3b). Shao *et al.* identify this species as THPC hydroxide (THPOH). Grayson and Hoffman recognize pentavalent THPOH as an intermediate in the conversion of THPC to THPO, but we observe only THPOH throughout the on-particle reaction. The adsorbed pentavalent phosphorane species is most likely sterically hindered by the Au surface, and the oxidation to THPO cannot reach completion (Figure S9). Additional off-particle evidence is consistent with the proposed mechanism, with ^{31}P NMR revealing the expected THPOH peak (δ , +36 ppm) after chemical degradation of THPC AuNPs by potassium cyanide (Figure S10). The X-ray photoelectron spectroscopy (XPS) data also agrees with the presence of an electronegative species that interacts with the phosphorus atom adsorbed to the particles (Figures S11–S13). The P 2p binding energy (BE) is revealed to increase from 131.7 eV to 133.0 eV one hour after THPC incubation. As BE increases, the shielding surrounding the phosphorus atom decreases due to the presence of an additional coordinated electronegative substituent. It is also worth mentioning that P^{V} THPC derivatives possess signature peaks above BE values of 132.5 eV.^[9] The ^{31}P NMR data along with the XPS analysis strongly suggests that the THPC is oxidized to a pentavalent THPOH species on-particle.

The hypothesized mechanism of spontaneous assembly and disassembly is depicted in Scheme 1. Induced by the large dipole moment on each particle that results from rapid citrate displacement,^[5f,k] the particles first rapidly assemble, triggering a red-to-blue color change. Upon adsorption, the Au surface renders itself as a catalytic substrate to convert THPC into THPOH on-particle. Evidence that the metal surface acts as a catalyst is supported by the extremely rapid self-assembly and disassembly of 20 nm citrate-stabilized AgNPs (Figure S14). With AgNPs, the particles return to their yellow color approximately 5 minutes after THPC addition, but ultimately aggregate minutes later. The kinetics of AgNP disassembly is orders of magnitude faster than that of THPC AuNPs, which is interesting considering Ag often exhibits differing catalytic activity relative to Au.^[10] AuNP disassembly only occurs when the pH is above the ligand pKa because the excess negative charge at the surface cannot hold the assembly together (Scheme 1b,c). The chains are ultimately broken apart into their monodisperse components, transitioning from blue to purple to red colors.

To further investigate this mechanism, it is hypothesized that tertiary hydroxyalkyl phosphines possessing neutral pKa values can experience similar assembly/disassembly properties relative to THPC. Many phosphonium ligands retain pKa values above 15, and this environment is not suitable for aqueous nanoparticles. The tertiary phosphines, tri(hydroxymethyl) phosphine (THP) and tri(hydroxypropyl) phosphine (THPP), were chosen because of their aqueous solubility and pKa values amenable to aqueous AuNPs. THP displays nearly identical assembly/disassembly behavior relative to THPC because their chemical structures are so similar (Figure 4a). THPP possesses a slightly higher pKa value of 7.2^[11] and the pH of the particle solution must be increased for the AuNPs to demonstrate disassembly characteristics similar to THPC (Figure 4b). At pH 6.3, complete THPP AuNP disassembly requires more than four days, whereas at pH 7.9, the particles approach monodispersity in no more than 24 hours (Figure S15). The ability to further support the hypothesis with tertiary hydroxyalkyl phosphines not only establishes versatility

with this approach, but also provides opportunities to develop a range of nanomaterial assemblies.

In this investigation, a spontaneous method for AuNP assembly and subsequent disassembly that requires no additives or stress-induced stimuli is demonstrated. Additionally, significantly less ligand is required to promote particle assembly and disassembly in comparison to high mM salt concentrations. The pKa of the hydroxyalkyl phosphine or phosphonium ligand plays an important role because the disassembly reaction is favored when the pH is above the ligand pKa. Manipulation of the THPC AuNP chains is accomplished by exploiting acid/base chemistry to finely tune the nature of the assembly, and this work provides a platform to develop advanced nanomaterial structures using various phosphine and/or phosphonium small molecules. Finally, the disassembly is most likely driven by the oxidation of the THPC ligand on-particle to the pentavalent THPOH species, which was identified in the first example of on-particle ^{31}P NMR spectroscopy on 15 nm gold colloids. The application of ^{31}P NMR spectroscopy to analyze ligand signatures on particles of this size offers an invaluable tool for exploring and understanding the role of phosphorus capping ligands adsorbed to nanomaterial substrates.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Spontaneous assembly and disassembly of 15 nm citrate-stabilized AuNPs (2.3 nM, pH 6.3, 2 mM sodium citrate buffer) induced by 100 μ M THPC. a) UV-vis spectra and resulting color changes. TEM images captured b) 5 minutes, c) 30 minutes, and d) 48 hours after THPC addition to the particles.

Figure 2.

HCl quenching of THPC AuNP disassembly. To four separate aliquots of 2.3 nM suspensions of citrate-stabilized AuNPs, 100 μ M THPC was added. Particle disassembly was quenched with 6.6 mM HCl at a) 30 minutes, b) 60 minutes, c) 4 hours, and d) 24 hours after THPC addition. The UV-vis spectra were monitored over 24 hours after HCl addition to determine particle stability, while TEM samples were prepared 24 hours after quenching with HCl.

Figure 3. ^{31}P NMR spectra of THPC in a) free solution and b) adsorbed to AuNPs. Particles are stored in 0.1M MES buffer containing 0.025% Tween 20 (pH 4.4).

Figure 4. Spontaneous assembly and disassembly of AuNPs induced by tertiary hydroxyalkyl phosphine ligands. a) UV-vis absorbance spectra of 100 μ M THP at pH 6.3 and b) 100 μ M THPP at pH 7.9.

Scheme 1.

Hypothesized mechanism of THPC AuNP assembly and disassembly. a) Upon reacting the citrate AuNPs with THPC, the particles immediately assemble into linear chains and slowly disassemble over the course of 48 hours. The temporary dipole moment of each particle created by the rapid displacement of citrate promotes particle assembly, but disassembly is only observed when the pH is above the pKa of the ligand. b) When the pH is above the pKa of THPC, the ligand is catalytically converted to a pentavalent phosphorane. c) These pentavalent THPOH isomers remain adsorbed to the particles and the excess negative charge cannot maintain the assembly, which breaks apart into monodisperse components.