

Exploiting Reducing Ability of DMF for Assembled Gold Nanostructures

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Abstract. We explore stable assembly of gold NPs in single step process by introducing a simple chemical synthesis in which pH changed gold precursor is added to dimethylformamide solution at RT. The redox chemistry of N, N-dimethylformamide (DMF) has been effectively utilized in the formation of surfactant free, small chain metal NPs networks (plasmonic oligomers) via molecular dipolar coupling. Kinetic absorption / TEM images illustrate gold nanocrystals formation, their inter-particle coupling as a function of pH as well as with DMF-Water ratio. Sub-nano gap inter-particle coupling b/w spherical/anisotropic Au NPs is seen through arising of new LSPR hump in NIR region. 1-D organized gold nanocrystals are formed when pH modified metal precursor is added to refluxed (80 °C) DMF: Water mixture. The inter-particle coupling provides unique strategy can promote complex sub-wavelength optical waveguides and nanophotonic devices.

Introduction

The formation of arrays of highly anisotropic 1D nanoparticles and their associated collective vector properties are of particular interest to nanoelectronics, optoelectronics, nanomagnetic and sensing devices biology [1]. The formation of chains resembling metal nanoparticles was prepared by physical confinement in grooves etched by ion beams in glass. [2] or porous anodic alumina, [3] and using a linear macromolecular or supramolecular matrix. Alternatively, a 1D matrix can be generated, in the absence of a model, by spontaneous self-assembly of isoelectric nanoparticles with intrinsic magnetic or electrical dipoles. In the second case, the linear assembly is induced by partial removal of the organic stable shell, which increases the electric dipole interactions between the particles. Metal nanoparticle chains have also been reported, [4-7] although the origin of the putative dipole interactions and chain assembly mechanism remains unknown. Unlike semiconductor quantum dots, face-centered cubic (fcc) metal nanoparticles have no intrinsic electrical dipole. However, surface charge and polarity heterogeneity, e.g. with heterogeneous spatial distribution of ligands limited on different crystal faces, [7-9] or with separation of nanophases in stable layers of mixed ligands, [10] is possible. motivation for anisotropic self-assembly.

Herein, redox chemistry of N, N-dimethylformamide (DMF) has been effectively utilized in the formation of surfactant free, small chain metal NPs networks via molecular dipolar coupling. This uniquely versatile and powerful chemical has been used as a solvent in a wide variety of synthetic procedures. In contrast to aqueous solution [11] where a reducing agent [12] is needed for initiating the nanoparticles [13] formation, DMF can itself reduce gold and silver ions partially or completely. The potentiality of reducing ability of DMF [14] for preparation of metal nanoclusters [15-17] is reported but with external energy sources [18]. The mechanism of the formation of metal

nanoparticles using the reducing power of DMF still remains a subject of controversy as literature reports predict that reeducation by DMF release CO₂ or carbonic acid [19] with dimethylamine [20] at room temperature, which doesn't have any detectable spectroscopic evidence [21-24]. Although the formation of Au nanoparticles [25] in DMF has already been reported, it seems to require catalysis by either poly(vinylpyrrolidone) [26,27] or by the metal seeds themselves. since Au seeds or PVP form complexes [28] with DMF molecules, they would strip off electrons from such complexed solvent molecules and act as catalysis. The important role played by DMF as a solvent and reaction medium in the formation of metal nanoparticles has motivated us in growth kinetics of metal NPs formation. We have pioneered the use of organic solvent which itself can serve as reducing agent as well as supporting medium and efficient formation of assembled gold nanostructures may not require the introduction of additional reducing agent unlike in conventional chemical methods [29]. Reactive DMF reduces pH modified HAuCl₄ at a faster rate via improved metal ligand exchange mechanism the inter-particle coupling provides unique strategy to promote complex sub-wavelength optical waveguides and nanophotonic devices.

Material and methods

Hydrochloroauric acid (HAuCl₄·3H₂O) was purchased from sigma Aldrich chemicals and DMF (N,N-Dimethylmethanamide), NaOH (Sodium Hydroxide), and other washing chemicals were purchased from Loba chemie Pvt. ltd.

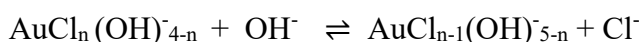
Experimental procedure

A solution 12 μl of 0.169 M aqueous HAuCl₃ was added to 500 μl (1000 μl) water followed by NaOH addition of different concentration as mention in graph. This mixture was added to DMF 4.5 ml (4 ml) DMF and put on sonication for 20 minutes under room temperature. As the reaction proceeded, the solution changed slowly in colour from light yellow to colorless to Apricot colour over few days.

However, the preparation method was partly modified in terms of heating process. A solution of 0.27 mM aqueous HAuCl₄ was added to 15ml of preheated mixture of DMF and water at 80°C and the mixture was refluxed by simply heating with vigorous stirring. As the reaction proceeded, the solution changed on color from light yellow to colorless to magenta color over few days.

Result and Discussion

We explore stable assembly of gold nanoparticles in single step process by introducing a simple chemical synthesis in which pH changed gold precursor is added to dimethylformamide solution at RT. The redox chemistry of N, N-dimethylformamide (DMF) has been effectively utilized in the formation of surfactant free, small chain metal NPs networks via molecular dipolar coupling. It has been observed that DMF has reducing ability in the basic medium for the metal ions, which is why it readily reduces AuCl₃ even at room temperature, whereas it cannot reduce HAuCl₃ (preferential solvation make the solution acidic in character). Hence the addition of a base like NaOH to a concentrated solution of Au⁺³ (HAuCl₄) results in the neutralization of its acidity, leading to the rapid formation of hydroxyl containing gold complexes as a result of stepwise substitution of Cl⁻. The addition of OH⁻ leads to the substitution of Cl⁻ ligands, according to reaction,



It was found that the reaction rate for formation of gold nanoparticles is affected by the pH of gold solution (with increase in pH NaOH reaction is faster). The chemical reduction of chloroauric acid to gold particles in the new reducing system therefore involves two step reaction process,

which are ligand substitution (Cl is replaced by OH) and chemical reduction of gold hydroxide species. As expected, the rate of ensuing nucleation process increases with increase in gold solution pH. The unusual UV- Vis spectra of as formed gold nanostructures at different pH modified metal precursor are illustrated in figure. 1.

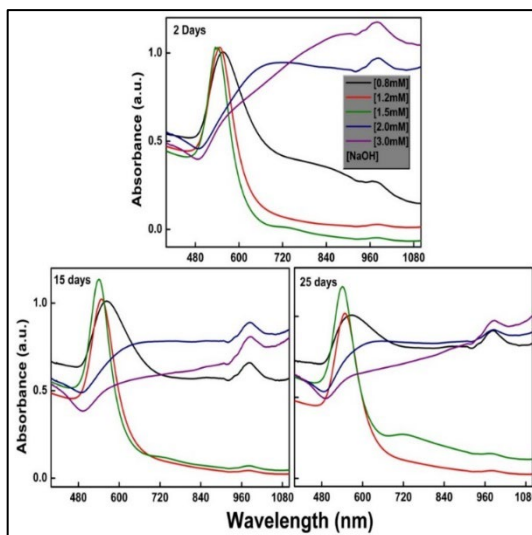


Figure 1. UV- Vis spectra of Gold nanoparticles obtained at different concentration of NaOH (resulting in pH modified Metal precursor) at DMF: water 9:1. Graph are normalize and translate vertically for better clarity.

Sub nano gap inter particle coupling b/w spherical Au NPs is seen (figure 2) through sequential LSPR shift from visible to NIR region arising due to dipole – dipole attraction further in confirmation with TEM images (figure 2). A new peak at 720 nm is observed (fig. 2) along with peak 540 nm (coincident with plasmon band of spherical particles) and intensity of this peak increase with time as shown in fig. 1 for NaOH at 1.5 mM sample.

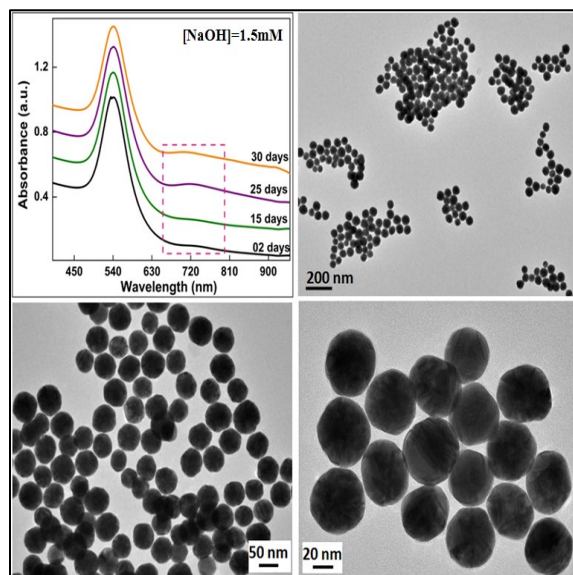


Figure 2. Kinetics absorption/TEM images illustrates assembled gold nanocrystal formation at DMF:water 9:1 and NaOH=1.5mM.

Arise of new peak is due to self-organization of 30nm spherical particles in 2-D array with subatomic between nearest particles can be seen clearly from the TEM image (fig. 2). And more organization is the intensity of longitudinal SPR and LSPR shifts towards red with increase in particle in array.

Furthermore, on increasing water content (take DMF: water ratio 4:1) we get assembly of anisotropic particles see fig. 3, instead of spherical as in low water see fig. 2. In this case anisotropic particle are formed and their assembly take place with time. Deviation from sphericity with decreased DMF to water ratio can result due to faster reducing ability of DMF in the presence of moisture.

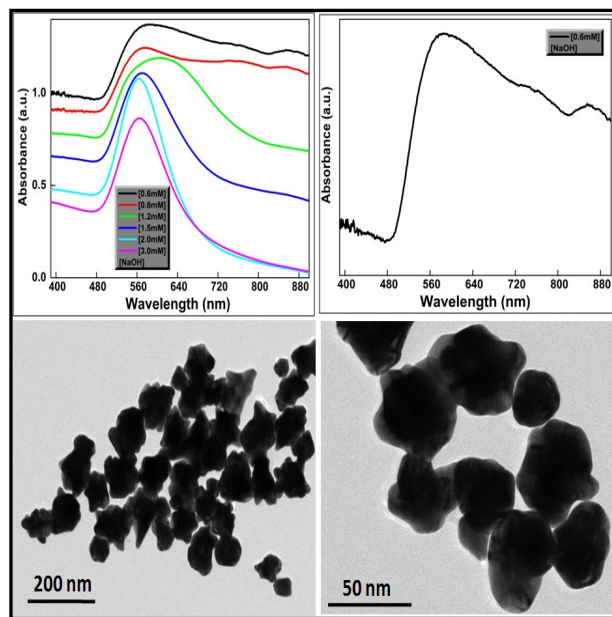


Figure 3. UV- Vis spectra and TEM images of Gold nanoparticles obtained at different concentration of NaOH (resulting in pH modified Metal precursor) at DMF:water 4:1. Graph are normalize and translate vertically for better clarity.

Kinetic absorption/ TEM images in fig. 4 illustrate the formation of 1-D organized gold nanocrystals formation where pH modified metal precursor is added to refluxed (80oC) DMF: water mixture. TEM image clearly depicts the inter particle coupling and small nanochain networks.

Dipole-dipole attraction from anisotropic distribution of residual surface charge on gold nanoparticles as well as from DMF molecular dimers drives the careful formation of 1D pearl-necklace morphology.

Our main focus is on the molecular interactions responsible for the growth kinetics of as formed nanostructures. The complex formation between DMF and pH modified gold species ensuing in the formation of the N – Methyl formamide ligand substituted chloroaurate complexes which further result in the surfactant free Au nanoparticles chain networks through formation of carbamic/ dimcarb acid in the presence of sufficient water under ambient condition

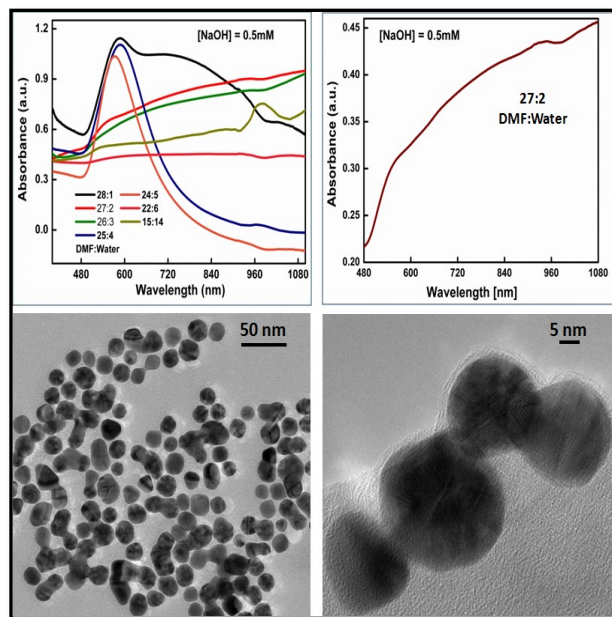


Figure 4. one dimensional self-organization of gold nanostructures obtained at different DMF and water ratio by refluxing at 80°C.

Conclusion

DMF maneuvers aggregation of as prepared spheroidal gold nanocrystals through selected facets even under RT aging, giving rise to small linearly twisted plasmonic gold chain networks, Composition of different gold (III) complexes with increasing pH controls its redox potential, crucial for the essential formation of stable assembled nanogold dispersions. The inter particle coupling provides unique strategy to promote complex sub- wavelength optical waveguides and nanophotonic devices.

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