



Dilution does the trick: Role of mixed solvent evaporation in controlling nanoparticle self-assembly



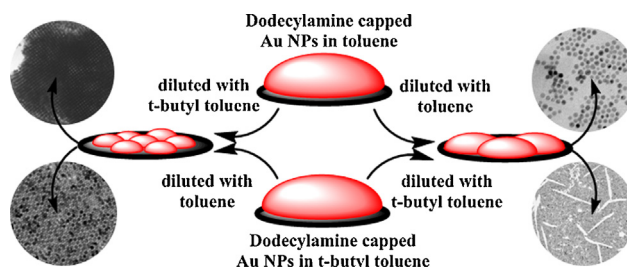
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HIGHLIGHTS

- Controllable dodecylamine capped gold nanoparticle superlattices have been obtained.
- Solvent evaporation from the nanoparticle dispersion leads to 2D or 3D superlattices.
- Dilution of dispersion with a similar but higher boiling solvent is a crucial step.
- Nature of superlattice structures depends on the differential solvent evaporation.

GRAPHICAL ABSTRACT



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ABSTRACT

An easy and convenient way to prepare superlattices of amine capped gold nanoparticles is presented. It is clearly established that solvent evaporation significantly influences the nature of resulting superlattices and critically governs whether monolayer or multilayer superlattices are formed. More specifically, it is demonstrated that dilution of the nanoparticle dispersion with a similar solvent (but with different vapour pressure) is an expedient handle to control the nature of self-assembly.

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1. Introduction

Self-assembly stands as an efficacious route to construct ordered nanoparticle architectures better known as superlattices [1–3]. Tunable optical, electrical and mechanical properties associated with these self assembled architectures find applications in diversified areas [4–6], and hence designing these structures have enthralled current researchers. Though a high level of control in directing self-assembly [7–10] has been achieved in last few

decades, there still exists greater prospect for investigations that can provide self-assembled architectures in a pre-desired manner.

Various methods have been proposed to direct self-assembly of nanoparticles (NPs) by tailoring chemical interactions between them or by using external fields, templates etc. [10,11]. Amongst the methods available, evaporation mediated ones stand out as extremely competent approaches to prepare highly ordered large area structures [12–15]. An efficient utilization of this method for desired self-assembles architectures requires thorough understanding of various aspects like diffusion and drying kinetics, interaction of the nanoparticles between themselves apart from their interactions with the substrates and solvents used and so on. This study attempts to provide a method to control the solvent

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evaporation and thereby control the ensuing self-assemblies. Gold NPs stabilised by a monolayer of thiol are one of the thoroughly studied systems in this respect [16–18]. The strong interaction between sulphur and gold renders great stability to the particles thereby assisting thiol monolayer to exist in an all-*trans* conformation [19,20]. Consequently this facilitates an interdigitation between the surface bound thiol molecules on adjacent nanoparticles leading to the formation of good quality SLs structures [21]. On the other hand, amine capped particles are not good choices as far as good SLs formation, though amine also forms nice monolayer over Au NPs [22] and imparts good stability to the dispersions. One of the explanations provided for this is the weak interaction between the amine head group and the gold surface compared to thiol [23], which allows exchange of ligands present in between nanoparticle surface and solvent. This makes the interdigitation between the amine molecules on the neighbouring nanoparticles to be an unfavourable process, hindering the SL formation.

We wanted to address this problem and therefore, in the present study, dodecylamine capped Au NPs were used as reference system. These were prepared by reducing AuCl₃ in presence of didodecylmethylammonium bromide (DDAB) surfactant in non polar solvents such as toluene or *t*-butyltoluene (referred as *tbt* later in the text). The as prepared polydispersed NPs were then converted to monodispersed ones using the digestive ripening procedure [24]. The particles obtained after digestive ripening are nearly monodispersed and remain suspended in the solvent without any apparent interparticle interaction. However upon drop casting on a TEM grid the particles self-assemble into different patterns. Great control over the nature of self-assembled structures (2D or 3D) could be achieved by controlling the solvent evaporation rates. It is important to note here that, the reference system used remains as a stable dispersion in the chosen solvent. Hence, the role of strong interparticle interactions as a predominant factor for self-assembly process is ruled out. Accordingly, these dispersion when drop casted on a TEM grid lead to the formation of randomly ordered (with toluene as solvent) or hexagonally closed packed (with *tbt* as solvent) monolayers. Interestingly when a drop made of dispersion from a mixture of solvents is allowed to dry on a TEM grid, dramatic changes in the nature of self-assembled structures could be seen. Since these solvents are similar in many respects, except in their boiling points and hence in vapour pressure (referred as *v.p.* later in text), this system provides a platform to study the evaporation effect systematically. Also the non-polar nature of both the solvents helps us to exclude the influence of other solvent related factors such as polarity (dielectric constants for toluene and *tbt* are 2.387 and 2.38 respectively at 20 °C), H-bonding etc. [25–29] on self-assembly process.

2. Experimental

2.1. Synthesis of Au NPs by digestive ripening method

Dodecylamine capped monodispersed Au nanoparticles were synthesized using well-known digestive ripening protocol [24] in two different solvent media i.e. *tbt* and toluene. 0.098 g of DDAB (didodecylmethylammonium bromide) was added in 10 mL solvent (toluene or *tbt*). AuCl₃ was dissolved in this by sonication to make a 0.01 M solution. The resulting dark orange solution was reduced by drop wise addition of aqueous NaBH₄ (40 μL, 9.4 M) under vigorous stirring for 1 h to ensure complete reduction. Dodecylamine was added to this colloidal dispersion maintaining metal to ligand molar ratio 1:30. Subsequently 30 mL ethanol was added to separate ligand coated nanoparticles from excess ligand, DDAB and other reaction side products. Precipitate was dried and re-dispersed in 10 mL toluene followed by the addition of another

portion of the ligand (1:30 metal to ligand ratio). The reaction mixture was then refluxed for 90 min at 110 °C.

2.2. Measurement of rate of evaporation

1 mL of solvent mixture (*tbt*: toluene ratio 1:3 and 1:5) were taken in two Petri dishes having same surface area and allowed to evaporate under room temperature condition. The weight change was measured using standard weighing microbalance under closed door conditions.

2.3. UV–vis spectroscopy

UV–vis absorption spectra of nanoparticle dispersions were measured using a Jasco UV–vis spectrophotometer (V-570 model).

2.4. Transmission electron microscopy

Samples for transmission electron microscopy were prepared by drop casting the nanoparticle dispersions on carbon coated copper grids (200 mesh). TEM analysis was performed on FEI, TECNAI G2 TF 30 and FEI, TECNAI G2 TF 20 instruments. Particle size distribution histograms were plotted taking 300 particles into account.

2.5. Optical microscopy

One drop of the solution containing the Au nanoparticle dispersion was placed on the TEM grid and examined using optical microscope (Leica) with 40× objective lens.

3. Results and discussion

The particle sizes were nearly independent of the solvent system used for the synthesis (Fig. ESM-1 and Fig. ESM-2). For understanding the dependence between nature of SLs obtained and the solvent evaporation from a mixed solvent system, the Au NPs synthesized in *tbt* were diluted with toluene by maintaining the solvent volume ratio of *tbt*: toluene as 1:3 and 1:5. Similarly Au NPs synthesized in toluene were diluted with *tbt*, maintaining solvent volume ratio of toluene: *tbt* as 3:1 and 5:1. For each of the above mentioned samples, UV–vis measurement showed characteristic peak of Au nanoparticles at ~525 nm (Fig. 1). No change was observed in λ_{\max} position and no broadening of peaks could be seen on diluting the toluene dispersed samples with *tbt* or vice versa. This confirmed that the nanoparticles were well dispersed in these solvents and no strong interparticle interactions exists [30].

However the TEM images obtained when a drop of these dispersions were allowed to dry on a TEM grid, were very different from one another. It was observed that particles synthesized in *tbt* on dilution with same solvent (5 times) formed uniform 2D monolayer extending over more than a micron length scale (Fig. 2a and b). The scenario changed completely, when the same sample was diluted with toluene. More specifically, dilution of the sample prepared in *tbt* with 3 parts of toluene afforded small islands of nanoparticles with preferential multilayer arrangement rather than a monolayer arrangement (Fig. 2c and d). Further increase in toluene volume ratio (*tbt*:toluene = 1:5) resulted in highly ordered 3D SLs (Fig. 2e and f). Similar results were also obtained when particles were synthesized in toluene and diluted with *tbt*. In this case too, at 3:1 volume ratio of toluene: *tbt* small domains of nanoparticles trying to assemble in an ordered manner (Fig. 3a and b) could be observed while the 5:1 volume ratio furnished good quality 3D fcc structure (Fig. 3c and d). These were exactly same to those obtained when particles synthesized in *tbt* were diluted with toluene and allowed to dry on a TEM grid. Very interestingly, when particles

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