Fabrication of Ordered Nanoparticle Arrays

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ABSTRACT

Gold nanoparticles of different sizes, 5nm and 10nm were synthesised in aqueous medium and subsequently transferred to organic phase after surface functionalisation with dodecanethiol. A novel method of fabrication of close–packed monolayer arrays of gold nanoparticles over an air-water interface was employed and effect of different experimental conditions was investigated. The arrays were stamped onto a silicon or quartz substrate by means of microcontact printing using polydimethylsiloxane (PDMS) stamp. Plasma treatment was employed as a method to remove the capping ligands, without disturbing their lateral order. Optimum plasma treatment conditions were identified for ligand removal. These ordered bare gold nanodots can serve as templates for fabricating ordered nanowires/nanotubes, which have potential for application in solar energy conversion, nanoelectronics etc..

Keywords: Gold nanoparticles, Ordered array, Plasma treatment

1. INTRODUCTION:

Nanotechnology deals with fabrication of nanostructures and its subsequent application as nanoscale devices. Generally fabrication of nanostructures can be classified as “top-down” and “bottom-up” approach. With “top-down” technology reaching its limit “bottom-up” approach has gained much importance [1]. Self assembly is considered as a promising “bottom-up” approach for fabricating nanostructures. The nanostructures find application in various fields like electronics, photonics, solar cells, as catalyst etc [2]. For nanoscale electronic devices, well ordered, patterned and addressable structures are required. Ordered nanowires, prepared from gold nanocatalyst, are important building blocks for next generation nanoelectronics as well as for

other applications. This research focuses on fabrication of ordered nanoparticle array that could serve as templates for nanowire growth and other devices, through a robust and simple method.

2. EXPERIMENTAL METHOD:

2.1 Synthesis Of Gold Nanoparticle:

Gold nanoparticles of 5nm and 10nm were prepared using protocol given by Slot et al [3]. 1ml of 1% (w/v) hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4.3H_2O$) solution was added to 79 ml of deionised(DI) water and heated to 60˚C. The reducing mixture was prepared by mixing 4ml of 1% w/v trisodium citrate dihydrate ($C_6H_5O_7Na_3.2H_2O$) and selected volumes (0.1ml for 10nm and 3 ml for 5nm) of 1% w/v tannic acid ($C_{76}H_{52}O_{46}$), and DI water to produce a final volume of 20 ml. In 10nm particle preparation 3ml of 25mM K_2CO_3 was added to reducing mixture to maintain pH. The reducing mixture was heated to 60˚C and added instantaneously into gold solution at 60˚C under stirring. The solution was maintained at 60˚C for 10min and 20min for 5nm and 10nm respectively. The mixture was further boiled for 10min. 35%v/v hydrogen peroxide, 0.1ml for 5nm and 1ml for 10nm, was added to remove excess tannic acid, boiled for 10 min and cooled. Then the aqueous gold sol was transferred into organic phase. 30ml of aqueous gold was added drop by drop into 1% w/v and 2% w/v of dodecanethiol $\{CH_3(CH_2)_{11}SH\}$ in ethanol for 5nm and 10nm respectively. The mixture was allowed to stand for 2 hr and then it was centrifuged at 3000rpm for 2hrs. Supernatant was removed and precipitate was washed with ethanol and dried. The dry precipitate was later redispersed in required organic solvent.

2.2 Preparation Of Nanoparticle Array:

Nanoparticle array was prepared by self assembly on air water interface as described by Santhanam et al [4]. A Teflon cell assembly (fig.1a and b) was used to obtain a concave surface of water. Water was slowly poured into the Petri dish containing Teflon cell until its level just touches the lower inside edge of the cell. Water gets pinned to the lower edge and then water is added drop wise to get required curvature. Gold nanoparticle suspended in organic solvent was added to concave surface till the rim of Teflon cell and the solvent was allowed to evaporate. The nanoparticle array was picked up on TEM grid, by Langmuir-Schaefer method, for

characterisation. It was also transferred to silicon wafer and quartz using microcontact printing with PDMS stamp as described by Santhanam et al [5].

2.3 Plasma Treatment Of Array:

The nanoparticle array was treated with plasma in Gatan plasma cleaner (Solarus 950). Plasma, a distinct state of matter, is basically an ionized gas composed of ions, electrons and other neutral species. The plasma process is typically maintained by the use of a low pressure, radio frequency induced gaseous discharge. Also, during the process the temperature ranges reached are low (30-70^{o}C), thus reducing the probability of particle coalescence. The gas used was mixture of oxygen and hydrogen with 27.5 sccm and 6.4 sccm respectively. The vacuum during the process is 450 mTorr. The power and time of treatment was varied according to requirement. Plasma treatment was performed on the array over TEM grid for TEM characterisation and on array over quartz for contact angle measurement. Contact angle of water droplet (3 µl) was measured at six different locations over the array surface using the sessile drop method and averaged. A Rame-harte goniometer was used for taking contact angle measurements. TEM characterisation of array was performed on TECHNAI G^2 F300 model

3. RESULTS AND DISCUSSION:

3.1 Synthesis Of Nanoparticles:

Gold nanoparticles of 5nm and 10nm size were prepared by method reported by slot et al [3]. On storage colour of 10nm particles change from red to brown and an extra peak corresponding to tannic acid was also observed in UV Visible spectrum. Tannic acid is likely to polymerise and hydrolyse on storage [6]. To remove excess tannic acid present in solution, H_2O_2 was added at the end of recipe and the mixture was further boiled for 10 min and cooled. Nanoparticles synthesised were characterised by UV visible extinction spectroscopy and TEM. UV visible spectrum, figure 2, shows the peak at 512nm for 5nm particles and at 517nm for 10nm particles. Gold nanoparticles were transferred to organic solvent after capping with dodecanethiol. 5nm nanoparticles were redispersed in n-hexane by sonication. But 10nm particles didn't get suspended in n-hexane. These particles remained as aggregates due to high Vander Waals attraction. Hence dispersion in other solvents like toluene, dichloromethane and chloroform were

examined. A mixture of n-hexane (75% v/v) and chloroform (25% v/v) was identified as best solvent to disperse 10nm nanoparticles.

3.2 Fabrication Of Nanoparticle Array:

Nanoparticle array was fabricated by Evaporation Driven Self Assembly (EDSA) on liquid air interface. The array formed is dependent on various factors like the concentration of nanoparticles in solvent and rate of evaporation of solvent. A set of experiments were designed to optimise the conditions required for fabrication of ordered array. The nanoparticle array was characterised by TEM. The theoretical area coverage of nanoparticles with observed interparticle distance in the array was calculated as 43.8% for 5nm and 49.9% for 10nm. The area coverage obtained from TEM image was compared with this ideal value. Lesser concentration of nanoparticles results in holes on the array and higher concentration results in multilayer of nanoparticles. The optimised conditions for fabrication of 5nm and 10nm array are given in table 1. A 100% ideal coverage could be obtained only if particles are highly monodisperse. Polydispersity in particles also gives rise to grain boundaries (change in orientation) and vacancies in array. Hence further tuning of array fabrication with highly monodispersed particles is to be done. This simple, easy, robust method to fabricate nanoparticles and transfer by microcontact printing could serve as alternate to conventional Langmuir-Blodgett method.

3.3 Plasma Treatment Of Nanoparticle Array:

The presence of capping ligands enhances the mobility of nanoparticle in array at high temperature and results in coalescence. Hence it is necessary to remove capping ligands without disturbing lateral order of array for using it as templates for nanowire growth and other electronic applications. Similar experiments have been demonstrated by Spatz et al [7] for removal of block copolymers from nanoparticle surface but with very less area density. Optimization of treatment parameters for both 5nm and 10 nm size range particle arrays was carried out. The arrays deviating from ideal behaviour, i.e. arrays with holes were also used for these experiments. The arrays were characterised with TEM before and after treatment and the results are summarised in table 2. Higher RF power and higher exposure time leads to coalescence of nanoparticles. This is due to reduction of thiol on surface and bombardment by ions. Exposure time was decreased,

starting from higher values, such that there is no disturbance in lateral order. After optimising conditions for 5nm and 10nm array as 20W, 10s and 50W, 10s respectively, array on quartz substrate was exposed to plasma at this parameter. The contact angle of water (3µl) on the array was measured before and after exposure to plasma and results are summarised in table 3. The contact angle of water on plain quartz is 33^{o} and on DDT SAM is 115^{o}. After plasma treatment, the contact angle decreases appreciably indicating the decrease in the hydrophobicity of the surface. This can only be due to decrease in area of exposed hydrocarbon chains and an increase in the gold/quartz surfaces (having lower contact angle). TEM studies show that at the optimized conditions, there is very little lateral movement/coalescence of gold nanoparticles, and so, these results indicate that DDT molecules have been removed, atleast from top surface of nanoparticles.

4. FUTURE WORK:

Fabrication of array using a highly monodispersed nanoparticles to eliminate vacancies and grain boundaries i.e. change in orientation within array. Arrays fabricated will be analysed by method comprising distance between particles and angle between neighbours such that even variation which could not observed visually could be identified and studied. Plasma treated array will be subjected to Fourier transform infra red spectroscopy to study the presence of dodecanethiol. Ordered nanowires are to be synthesised using this bare gold nanoparticle array templates.

5. CONCLUSION:

Gold nanoparticles of desired size were prepared in aqueous base using Slot et al protocol mand then phase transferred to organic solvents using dodecanethiol. Nanoparticle array was fabricated by self assembly using a simple and robust method. Conditions were optimised to get an ordered array. Arrays were transferred to quartz and silicon substrate using microcontact printing. Arrays were exposed to plasma to remove capping ligands without disturbing lateral order and optimised conditions for different sizes were obtained. These ordered nanoparticle arrays with bare metal surface could serve as templates for nanowire growth which has potential application in solar cells, nanoelectronics etc.

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Table 1: Optimised concentrations for fabrication of nanoparticle array

Nanoparticle size nm	Solvent	Nanoparticle concentration particles/ml
~5	n-hexane	1 E14
~10	75%v/v n-hexane and 25%v/v chloroform	1.2 E14

Table 2: Parameters of plasma treatment of array

S. No.	Size range	Power W	Duration s	Distribution of plasma power* s	Remarks
1	5nm	50	30	single	Lateral order disturbed
2	5nm	20	40	15<20>15<20>10	Lateral order disturbed
3	5nm	20	30	single	Lateral order disturbed
4	5nm	20	20	10<30>10	Lateral order disturbed
5	5nm	20	15	5<15>5<15>5	Lateral order undisturbed
6	5nm	20	10	5<15>5	Lateral order undisturbed
7	10nm	10	20	10<30>10	Lateral order undisturbed

8	10nm	50	30	10<30>10<30>10	Lateral order disturbed
9	10nm	50	15	5<15>5<15>5	Lateral order disturbed
10	10nm	50	10	5<15>5	Lateral order undisturbed

**the distribution plasma power is: cleaning time<rest time>cleaning time; single implies no rest time*

Table 3: Contact angle of water on array before and after treatment

S.No.	Experiment details	Plasma Conditions (Power, Exposure time)	Contact angle(degrees)	
			Before Plasma	After Plasma
1.	Array(5nm size range)	20W, 15sec	84±3.5	47±2.9
2.	Array(10nm size range)	50W,10sec	88±7.6	60±6.9

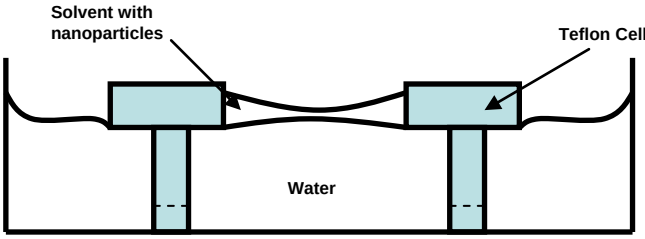

Figure 1a

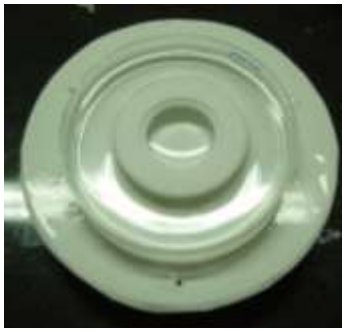

Figure 1b

Figure 1a & b: Teflon cell

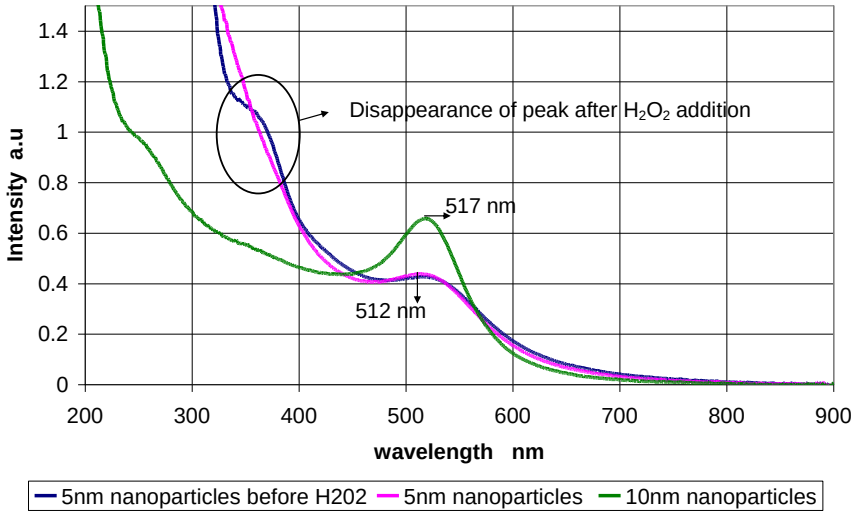

Figure 2: UV visible extinction spectrum of aqueous gold nanoparticles

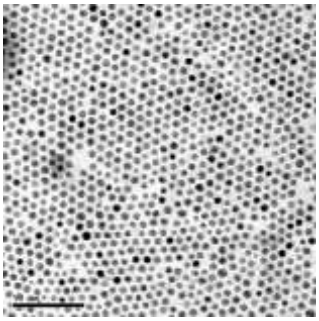

Figure 3a
Area % = 38.8%
% Ideality = 88.6%
Particle size: 4.9±0.61nm
Scale bar: 50nm
Magnification :75,000X

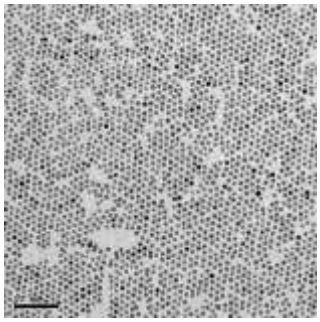

Figure 3b
Area % = 36.3%
% Ideality = 82.9%
Particle size: 4.9±0.44 nm
Scale bar: 50 nm
Magnification: 49,000X

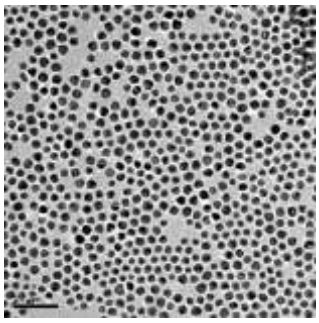

Figure 3c
Area % = 41.4%
% Ideality = 83.1%
Particle size: 9.4 ± 1.10
Scale bar: 50nm
Magnification: 49,000X

Figure 3: TEM images of nanoparticle array

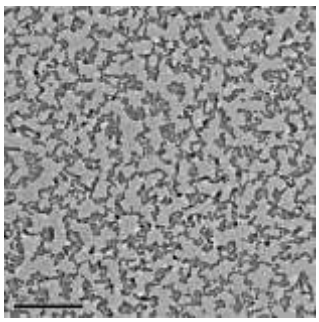

Figure 4a
5nm array
Power: 50w
Duration: 30s

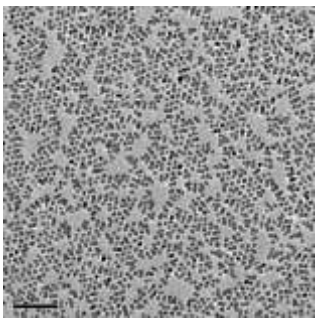

Figure 4b
5nm array
Power: 20w
Duration: 20s

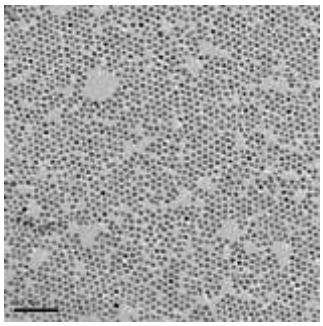

Figure 4c
5nm array
Power: 20w
Duration: 10s

Figure 4: TEM image of plasma treated 5nm array (scale bar: 50nm and magnification: 49,000X)