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Taguchi Optimization Method for Tuning Aspect Ratios for Synthesis of Gold Nano Rods

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ABSTRACT

This research account is an attempt to apprehend the important parameters for synthesizing monodispersed Gold nano rods (GNR) of desired aspect ratios. There is plethora of synthetic strategies for the synthesis of GNR amongst which seed-mediated one is the most celebrated one since it is simpler and is capable of synthesizing GNR of desired aspect ratio. But the biggest hurdle is to standardize all the parameters such as concentration of gold chloride, CTAB, AgNO3 and pH for GNR synthesis and also comprehend the most accentuating and key parameters which affects the most. This is possible only with the help of a Taguchi L9 Orthogonal array design which is a statistical tool to optimize the parameters and also find the percentage effect of each parameter. The S/N ratio which was selected for the synthesis of desired aspect ratio was 'smaller the better' which could assist in the synthesis of GNRs of desired aspect ratios. After optimization the most influential parameters for GNR synthesis is found to be 0.5mM Gold, 0.2M CTAB, 5mM Silver nitrate and 3.1 pH.

Key Words: Gold nano rods (GNR), CTAB, Aspect Ratio.

INTRODUCTION

Gold nanoparticles exhibit unique size and shape-dependent properties which is conspicuously seen in colours ranging from wine red to blue color as a consequence of quantum confinement effect. The burgeoning interest in anisotropic structures such as rods, triangles, cubes due to their enigmatic applications has led to the scientific endeavour. Gold nanorods (GNRs) need special contemplations since they exhibit relative stability and optical properties over other anisotropic structures, thus exhibiting avalanche of applications in catalysis, optoelectronics, optics, single electron transistors, nonlinear optical devices, photo-electro chemical applications, cancer treatment, markers for TEM and SEM, Nano-electronics and Nano-chips [1] . They possess two localised surface plasmon peaks i.e. transverse surface plasmon peaks (TSPR) and longitudinal surface plasmon peaks (LSPR). The LSPR peak is more sensitive to aspect ratio of the nanorod and is red shifted from visible to infra red region with increasing aspect ratio. The aspect ratio of GNRs can be tuned based on their optical extinction spectrum. Towards extension of Mie theory, relationship between extinction coefficient and aspect ratio for prolate ellipsoid which is in approximation to nanorods is given [2] . The aspect ratio is the function of different parameters such as temperature, pH, and concentration of reactants and the dielectric constant of the solvent used for synthesizing GNRs [3] . The scattering efficiency of the GNRs is proportional to wavelength of light as well as aspect ratio. The absorption efficiency is dominant for smaller rods and scattering efficiency is dominant for larger rods keeping fixed aspect ratio.

The different strategies for the synthesis of GNR include template method, electrochemical method, Seed-mediated method, photochemical method and several others. The most celebrated and simple method to fabricate GNRs is seed mediated. This method is most effective in producing high yield nanorods. Towards this endeavour, material scientists have synthesized gold nanorods using citrate stabilized Gold nanoseeds [4]; CTAB (Cetyl trimethyl ammonium bromide) protected Gold nanorods using gold seeds [5] synthesized by Sodium borohydride; a modified the seed mediated method of GNRs synthesis which exploited AgNO3 for one-dimensional growth of GNRs is also tried [6].

Our group has also been working on perfecting the synthesis of GNR of desired aspect ratio and monodispersity. During our endeavour we have realized that though aspect ratio of GNRs can be tuned by varying sensitive parameters such as the concentration of Gold chloride, temperature, pH and solvents as aforementioned, the selection of these reaction conditions as a whole often becomes a daunting task. To unravel such mysterious problems, a statistical treatment considering all the important parameters in a hierarchy becomes mandatory.

Taguchi methodology - In the present work, an attempt has been made to comprehend the different variable parameters involved in gold nanorod synthesis and impact of each parameter on the overall reaction during the formation of GNRs. This has been achieved by Taguchi Orthogonal array method which is used as a tool to select the desired aspect ratio of GNRs by manipulating a combination of design variables. The S/N ratio is a statistical operation which selects the best combination of the design variables. The L9 Taguchi design was exploited to study the effect of variables such as gold ion, CTAB, $AgNO_3$ concentrations and pH. The impact of these variables on the aspect ratio of GNRs was studied using Taguchi design to investigate the effect of different operational factors on the overall response of the aspect ratio of GNRs using nine experiments with logical combinations of parameters in an orthogonal array.

To the best of our knowledge, this is the first evidence of parametric optimisation of aspect ratio of GNRs using Taguchi method as a statistical tool to find out the most optimum parameters. The present work is an attempt to comprehend the optimum parameters for GNRs synthesis using Taguchi array as well as the percentage effect of each parameter on overall synthesis of GNRs of desired aspect ratio.

MATERIALS AND METHODS

Materials

Chloroauric acid ($HAuCl_4$, Molecular Weight 393.79g mol), sodium borohydrate (NaBH4), ascorbic acid, silver nitrate were obtained from Sigma Aldrich, USA. All the glassware were washed with aqua regia and experiments were performed in Nanopure water (18MΩ). GNRs synthesis was done using seed mediated method [7]

Characterization

The spectrophotometric analysis of the colloidal solutions containing GNR was carried out using Perkin Elmer (Lambda 25) UV-VIS spectrophotometer. Morphological details of the synthesized GNRs were studied using Transmission Electron Microscope (TEM) (Zeiss Microimaging GmbH, Germany) and FEG-Scanning Electron Microscope (SEM) (Zeiss Microimaging GmbH, Germany). All samples were centrifuged (REMI) at 5000rpm and then both the side walls and sample present at the bottom of the centrifuge tube were separated and then placed on formvar coated copper grid for TEM analysis and on silicon wafer for SEM.

Preparation of the seed

2.5 ml of 1mM of HAuCl4 was added to 5ml of 0.2 cetyl trimethyl ammonium bromide (CTAB). To this solution 600µl of pre-chilled 10mM Sodium borohydride ($NaBH_4$) was added under vigorous stirring condition forming pale yellow coloured solution. The experiment was performed at 20^0 C using Nanopure water (18MΩ).

Preparation of the growth solution

Growth solution for GNRs was prepared by 2.5ml of 1mM HAuCl4 in 2.5ml of 0.2M CTAB. To this solution, 113µl of 4mM $AgNO_3$ and 35 µl of 78.8mM ascorbic acid were added followed by gentle agitation forming a transparent growth solution. 4µl of seed solution was transferred into unstirred growth solution and the reaction was allowed to take place for 2 hrs.

Taguchi design of experiments

Taguchi method for optimization of parameters was followed [8].The selection of the parameters was based on our previous works on parametric optimization of GNRs for photothermal therapy. The design of the experiments was done using four different parameters which are mutually exclusive (Table 1). L9 orthogonal array was used to set up the experiments (Table 2). The three parametric levels were selected in such a way that a desired value of aspect ratio of GNR is derived. As a matter of fact, the smaller the better factor was signal to noise ratios (S/N ratio) were used for the determination of the percentage impact of each parameter on GNR synthesis viz., smaller the better. The calculations done were as follows:

$$S / N = 10 \, Log \frac{\text{Square of means } (y^2)}{Variance \ (v)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(3)}$$

Where y is the mean response calculated as $y = (\frac{1}{n} \sum y_i)$

And v *represents the standard deviation expressed as*

$$v = \sqrt{\sum \frac{(y_i - y)^2}{(n-1)}}$$

Table 1- Different parameters and levels used, to design orthogonal array

Parameters	Level 1	Level 2	Level 3
A. Gold salt Conc.	0.5mM	1 mM	1.5mM
B. CTAB	0.2 M	0.3 M	0.4M
C. $AgNO_3$	3mM	4mM	5mM
D. pH	2.5	3.5	4.5

The different parameters involved in designing desired aspect ratio of GNRs are Gold salt, CTAB, AgNO3 concentration and pH. In the present work, the temperature of the reaction system was kept at 20°C which is found to be optimum based on our previous results. Three different concentrations of Gold salt (0.5, 1.0, 1.5M), CTAB (0.2, 0.3 and 0.4M) and $AgNO_3$ (3, 4 and 5mM) were considered and different pH (2.5, 3.5 and 4.5) were also selected. L9 Orthogonal array.

Table – 2: L9 Orthogonal table as per Taguchi method for GNR Synthesis

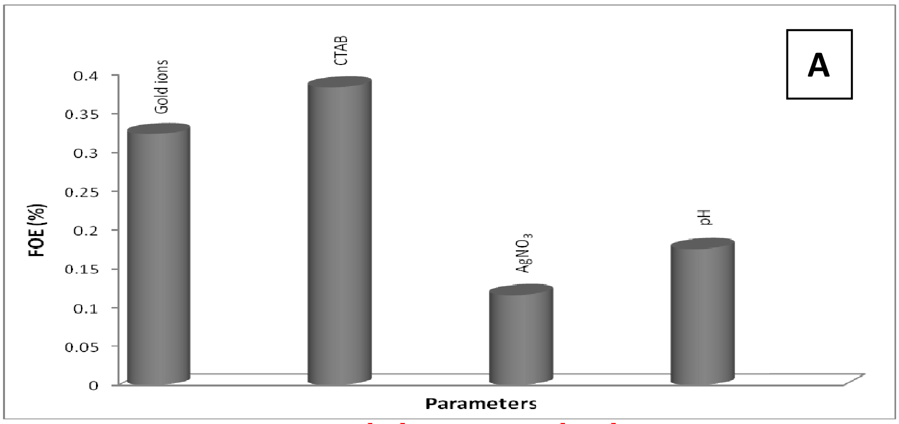
Exp. No.	Gold salt A	CTAB - B	$AgNO_3$ – C	pH – D
L-1	0.5mM	0.2 M	3mM	2.5
L-2	0.5 M	0.3 M	4mM	3.5
L-3	0.5mM	0.4M	5mM	4.5
L-4	1 mM	0.2 M	4mM	4.5
L-5	1 mM	0.3 M	5mM	2.5
L-6	1 mM	0.4M	3mM	3.5
L-7	1.5mM	0.2 M	5mM	3.5
L-8	1.5mM	0.3 M	3mM	4.5
L-9	1.5mM	0.4M	4mM	2.5

RESULTS AND DISCUSSION

Taguchi Design and Optimisation:

The parametric comprehension for GNR synthesis and an attempt to quantitatively study the impact of individual parameter in overall synthesis has led to the exploitation of statistical support system such as Taguchi Design. This design of experiment has got a daunting task of selecting the best parameter for synthesis of GNRs of desired aspect ratios. Since the object of this work was to find the best conditions for the synthesis of monodispersed GNRs of smaller aspect ratio relevant for photo-thermal therapy of cancer, signal to noise (S/N) ratios were calculated assuming the "smaller the best" condition [8].

The parametric optimization of all the variables for the criteria smaller the better exhibited 0.5mM gold ions, 0.2 M CTAB, 5mM AgNO3 and pH 3.5, to be effective for GNR synthesis (fig - 1). This is in accordance with the experimental results as shown in table (table 1).



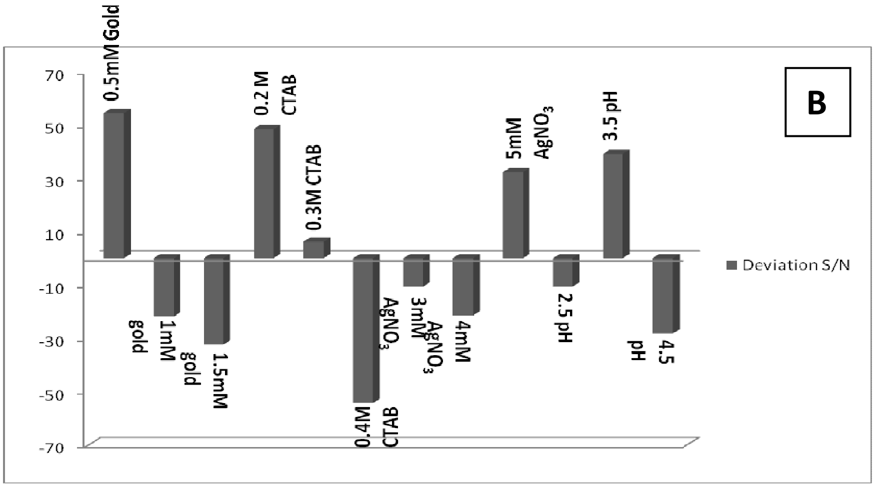


Figure – 1: Showing (A) % impact of each parameter on the GNR synthesis and (B) S/N ratio of parameter impact as per smaller the better calculations of Taguchi method (yellow –gold, white CTAB, grey – silver and red – pH)

The above figure (considering Smaller the Better S/N ratio) shows horizontal axis having different levels of each significant factor and the vertical lines indicates the trend of each parameter at different levels.

Considering smaller the better as a criteria for determining the smaller aspect ratios, it was found that the optimum conditions for designing GNRs of 3.5 to 4 aspect ratio , were 0.5 mM of Gold ions, 0.2 M of CTAB and 5 mM of $AgNO_3$ at 3.5 pH. Gold ion conc. was kept at the helm of GNR synthesis i.e. at level 1, CTAB at level 2, pH at level 3 and $AgNO_3$ at level 4. However, these calculations illustrate deviations from S/N ratio which are incapable of showing an impact of each parameter on the aspect ratio of GNR. Thus, to investigate the % influence of these levels and parameters on the smaller aspect ratios, "effect of factor of each parameter" (FOE %) were calculated. The most influential parameters for smaller aspect ratios were CTAB 38.41 %, Gold ions 32.37 %, pH 17.56 % and $AgNO_3$ 11.63.

The optimization of GNR synthesis was performed for smaller aspect ratios. It was deciphered that **CTAB** has a major role to play in GNR formation. It was found to be optimum at 20 C which is also the "Kraft point" for CTAB allowing single layered micelle formation. Within this micelle, 1D crystal growth of nanorod is possible. Further, the role of CTAB is to form strong metalo-micellar complex, protecting instant reduction of Au^{+3} by caging the complex inside the micelle. The vectorial growth of GNR is the resultant of preferential adsorption of CTAB on 110 facets inhibiting any extra growth at 111 facets of GNR leading to disciplined elongation of GNRs.

The next most imperative armamentarium is **Concentration of Aurochlotic Acid**. The ratio of CTAB: Au^{+3} were found to be 400:1, which is optimum for regulated growth of nanorods.

It was contemplated that **pH** is also one of the most influential parameter for GNR synthesis. At inherent pH (2.5 - 3), UV Vis spectrum of the growth solution shows both TSPR and LSPR peaks. The Gaussian shape of LSPR is sharpened at this pH which is an indicator of uniform and monodispersed GNR.

The shape and size of the nanoparticles were further confirmed using TEM (Fig. 1 and 2) which indicates rods of smaller aspect ratio with flat tips. As we increase the pH to 4.5, the morphology of GNR becomes bone shaped (Fig.) leading to the reduction of the aspect ratios. pH plays a cardinal role in the tailoring of GNRs due to the slow reducing capacity of ascorbic acid. The weak reduction potential of ascorbic acid at lower pH results in the reduction of the Au^{+3} to Au^{+1} which is further reduced to Au^{0} on addition of seed solution. Moreover, the weak reduction potential of ascorbic acid at lower pH is not capable enough to reduce silver ions to Ag^{0} leading to the formation of AgBr [9] which binds at specific facets leading to directed growth of GNRs.

The optimum concentration of **Silver Nitrate** was also determined to be 5mM which is responsible for directed growth and assembly of GNRs in the presence of CTAB. AgBr has a dominant role to play in the synthesis of GNRs by getting deposited on 110 facets of GNR surfaces at the gold- CTAB complex.

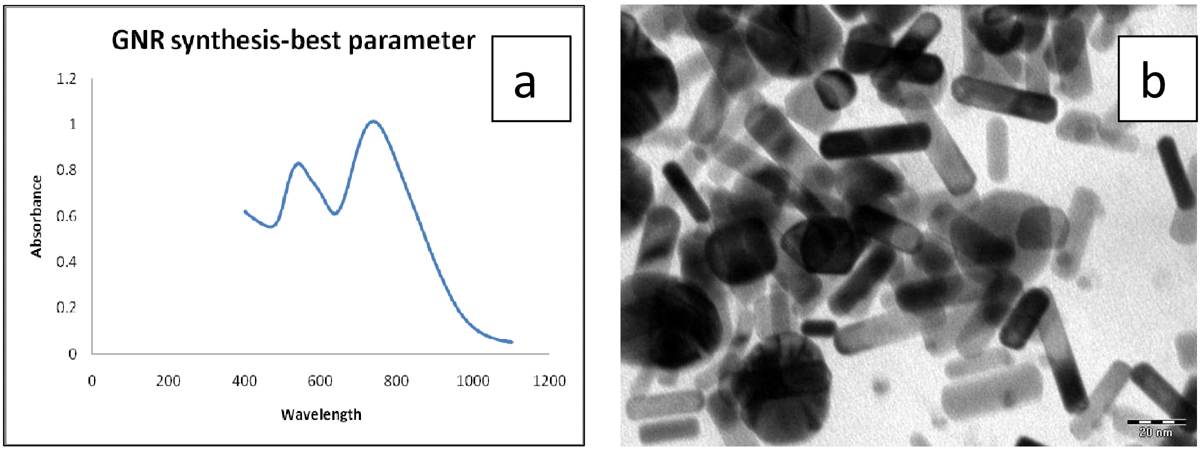


Fig 1 – (a) UV spectra of GNR synthesized under all optimal parameters (i.e. 0.5mM gold ions, 0.2 M CTAB, 5mM AgNO3 and pH 3.5) and (b) TEM of gold nanoparticles showing spherical as well as rod shaped structures

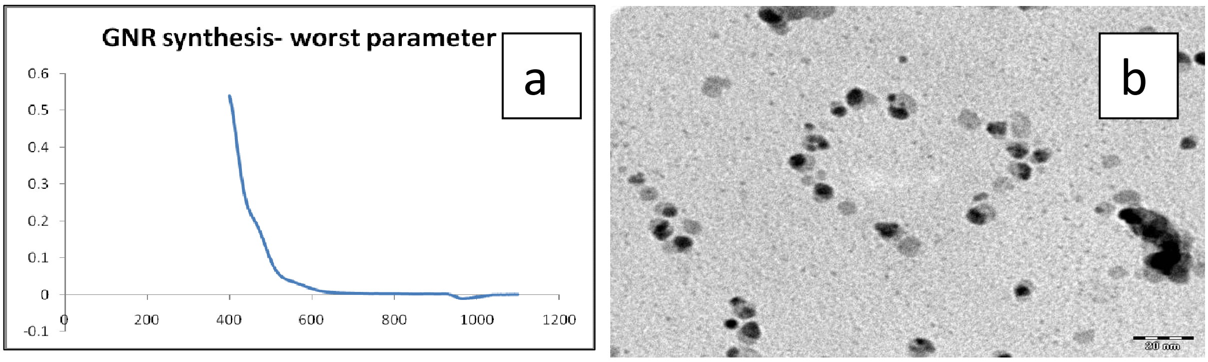


Fig.2 (a) UV spectra of parameters (1.5 mM gold chloride, 4mM AgNO3, 0.5M CTAB & pH 4.5) that failed to yield GNR, instead produced only spherical gold nano particles. (b) and Transmission electron micrograph of spherical gold nanoparticles

An attempt was done [10] to proposed a model derived from Taguchi model to predict the mean size of the particles as well as the width of the corresponding size distribution . Following the same model, (parameters were optimised for the synthesis of flower like cobalt nanostructures under the influence of microwave radiation [11].

It must be mentioned here that our attempt has yielded a mixture of GNR and spherical gold nano particles. We have standardized a method to separate out the GNR from a mixture of muti-shaped gold nano particles using centrifugation (in press)

CONCLUSION

Taguchi optimization has helped in deciding the best parameters for the synthesis of moderate aspect ratio of GNR which we propose to study for their suitability for photothermal therapy of cancer.

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