Amino acid Mediated Synthesis of Different Structural Gold Nanoparticles

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MP18005

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Certificate of Examination

This is to certify that the dissertation titled "**Amino acid Mediated Synthesis of Different Structural Gold Nanoparticles**" submitted by Mr. Abhinil Ghosal (Reg. No. MP18005) for the partial fulfilment of MS degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Santanu Kumar Pal	**Dr. Angshuman Roy Choudhury**	**Dr. Subhabrata Maiti (Administrative Guide)**

30.04.21

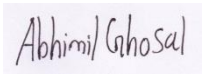
Dr. Debrina Jana (Supervisor)

Dated: 30/04/2021

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Debrina Jana at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography



Abhinil Ghosal

(Candidate)

Dated: 30.04.2021

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Debrina Jana

(Supervisor)

Dated: 30.04.21

Acknowledgement

Unlike every year, this time, the research was more challenging as the world is facing the Covid-19 pandemic, and due to a long lock-down, my research was hampered. In the year of this crisis, my Supervisor, Dr. Debrina Jana, continuously helped me, inspired me, and guided me for research by maintaining all the Covid-19 safety measures. I am blessed to have a supervisor like her. I want to express my sincere gratitude to her.

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I want to thank all of my family members, friends, teachers, and well-wishers for supporting me.

List of Figures:

Notation and Abbreviations

NPs	Nanoparticles
TEM	Transmission Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
CD	Circular Dichroism
CTAB	Cetyl Trimethyl Ammonium Bromide
AA	Ascorbic acid
TA	Tannic acid
PVP	Polyvinylpyrrolidone
$HAuCl_4$	Chloroauric acid
THH	Tetrahexahedron
$AgNO_3$	Silver nitrate
Cys	Cysteine
$NaBH_4$	Sodium borohydride
Pd	Palladium
Ag	Silver
Au	Gold

Contents

Abstract

In the edge of inter-disciplinary, plasmonic nanoparticle chemistry is one of the versatile topics as it connects several fields from optics to nanomedicine. Though nanoparticles chemistry brings science and technology to the next generation, the chemistry behind the nanoparticles' formation is still not revealed properly due to the lack of instrumentations. From the 1850s to the present day, several researchers synthesize different types of plasmonic nanoparticles as the plasmonic, sensing, catalysis all properties are highly dependent on the size and shape of the nanoparticles. Sharp-edged, high index facets nanoparticles are demanded for catalysis and sensing purpose, whereas different nanoparticles with different LSPR peak is needed for optics. Small size nanoparticles are extremely good for catalysis, SERS sensing, whereas big size nanoparticles are wanted for nano-bio chemistry. Hence, the synthesis of plasmonic nanoparticles is still significant.

In the first project, the intention was to develop the approaches to synthesize single chiral nanoparticles by using amino acids on small size nanoparticles having high index facets. The single chiral nanoparticles were discovered (in 2018 by Prof. Ki Tae Nam), where chiral, thiol-containing amino acids were used on the nano seed to observe chirality. Here the same experiment has been performed on tetrahexahedron seed to get chiral nanoparticles. Another new approach has been performed to use a concave cube as a seed and was treated it with a chiral growth solution.

In the second project, the differently shaped and size-containing nanoparticles were synthesized in a one-step reaction by using PVP as a capping agent. Following one established reaction by Prof. OOK Park, several modifications like varying concentration, volume, capping agent, reaction times, etc have been done. The unique approach was to use amino acids in the reaction to observe the changes in product structures. PVP is a comparatively cheap and available surfactant than CTAC or other expensive surfactants. Here the most common solvent DMF performed the role of solvent as well as reducing agent simultaneously.

Project- 01

Approach to Synthesis of Chiral single Nanoparticles

INTRODUCTION

Plasmonic Metal Nanoparticles:

The light-matter interaction has attracted significant attention of the science communities, and the concept of plasmonic nanometals[1] is one of the essential aspects of it. Although numerous important developments have been observed in this vast research area, there are still many unexplored areas available for researchers to work on. Briefly, the plasmonic nanoparticles are those that can couple with electromagnetic radiations. Unlike the macroparticles, the electron density of these nanoparticles are localized on the surfaces, which interact with electromagnetic (EM) radiation, and show spectral characteristics in UV-Visible region of the EM radiation.[2] The interactions between electromagnetic waves and nanomaterials lead to the generation of a dipole polarization on the surfaces if the frequency (resonate frequency) of the electromagnetic wave is equal or higher than the natural wave frequency of the metal particles.

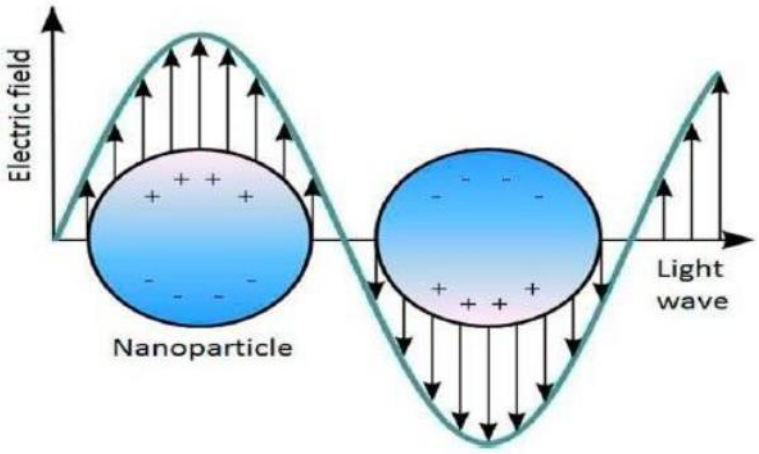


Fig 1. Schematic representation of the interaction between Electromagnetic wave and the nanoparticles (Reproduced from Reference 2).

As the resonance frequency of noble metal lies in visible region, they show beautiful colors in the solution. Despite the same metal nanoparticles, the color of the solutions is different, and characterization UV peaks also. The color of the nanoaprticles depends on the shapes and sizes despite of containing same chemical components. The change in the sizes and shapes of nanoparticles alter the electron densities and resonate wavelength.

Besides the sizes and shapes, the color especially depends on the dielectric constant of the dispersing medium.

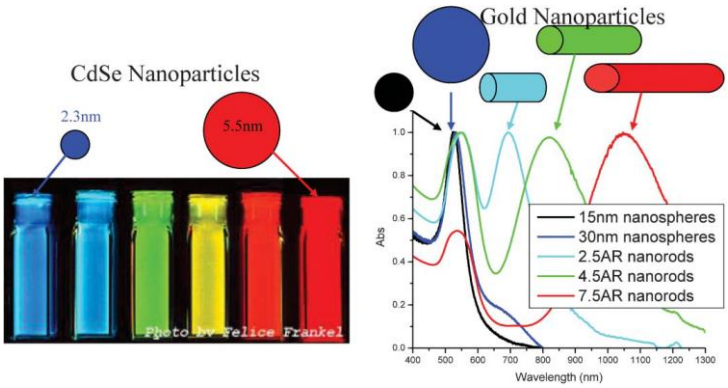


Fig 2. Representation of the LSPR peaks of different sized same nanoparticles. (reproduced with permission from ref. [3])

Chirality:

As the detection and separation of chiral molecules are not possible in achiral or usual environments, chirality is one of the most important and demanding topics in chemistry. Numerous numbers of researchers are working on chiral chemistry as it is the 'holy grail' of applied as well as basic chemistry. Extending the concept of chirality from organic,[4] and inorganic chemistry, [5] and material science,[6] chemists are also exploring for several applications like sensing,[7] enantioselective catalysis,[8] etc. Chiral molecules can rotate the vector of plane-polarized light either clockwise or in the anticlockwise direction. Further, scientists developed easy and alternative chirality definitions where they claimed that chiral molecules must not have superimposable mirror images. In terms of mathematics, chiral molecules must not have any center of symmetry or any sigma planes.

Although the concept of chirality was introduced based on chiral center, it has been observed in axial chirality,[9] chiral plane,[10] and even in chiral nanoparticles. Substituted allene, biphenyls etc shows axial chirality, whereas substituted ferrocene shows planar chirality. The chirally opposite isomers are called enantiomers which show the exact and equal deviation of plane-polarized light but in the opposite direction. Chirality of molecules can be detected by polarimeter and Circular Dichroism instruments.

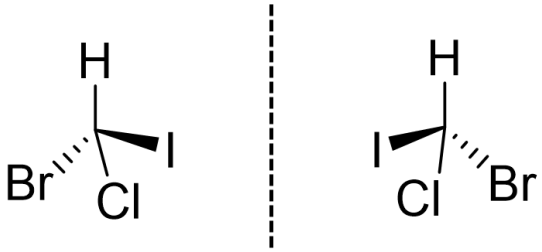


Fig 3. Examples of a chiral molecule and enantiomer

Chiral Nanoparticles:

Plasmonics nanoparticles have found diverse applications in chemistry, especially in catalysis,[11] sensing,[12] optics,[13] forensic sciences,[14] negative refractive indexes,[15] polarization control,[16] but the limitations lie in selectivities. Although researchers have started to enhance selectivities for catalysis reactions by using different types of capping agents, stabilizing agents but enantioselectivity is still a potential big challenge for science communities. In the field of heterogeneous catalysis[17], the separation of products from catalysts is much easier than homogeneous catalysis, but the selectivity is not so pronounced. There are lots of nanostructures that are synthesized intentionally or mistakenly, can be chiral if the shape doesn't contain center of symmetry. So the challenge does not lie in synthesizing chiral nanoparticles but is in the homogeneous synthesis of chiral structures having identical chirality. The concept is not limited to identical chirality; also, the goal is further extended to the enantiomers of nanoparticles, showing exactly opposite chirality.

Several approaches are developed often for chiral introductions like surface chirality,[18] self-assembly,[19] ligand-mediated chirality,[20] superstructures,[21] or single chiral nanocrystals. Lan *et al.*, improvised the concept by using DNA origami and keep the two gold nanorods on two different faces of origami without having any direct contact between two gold nanorods in a 3D architecture.[20]

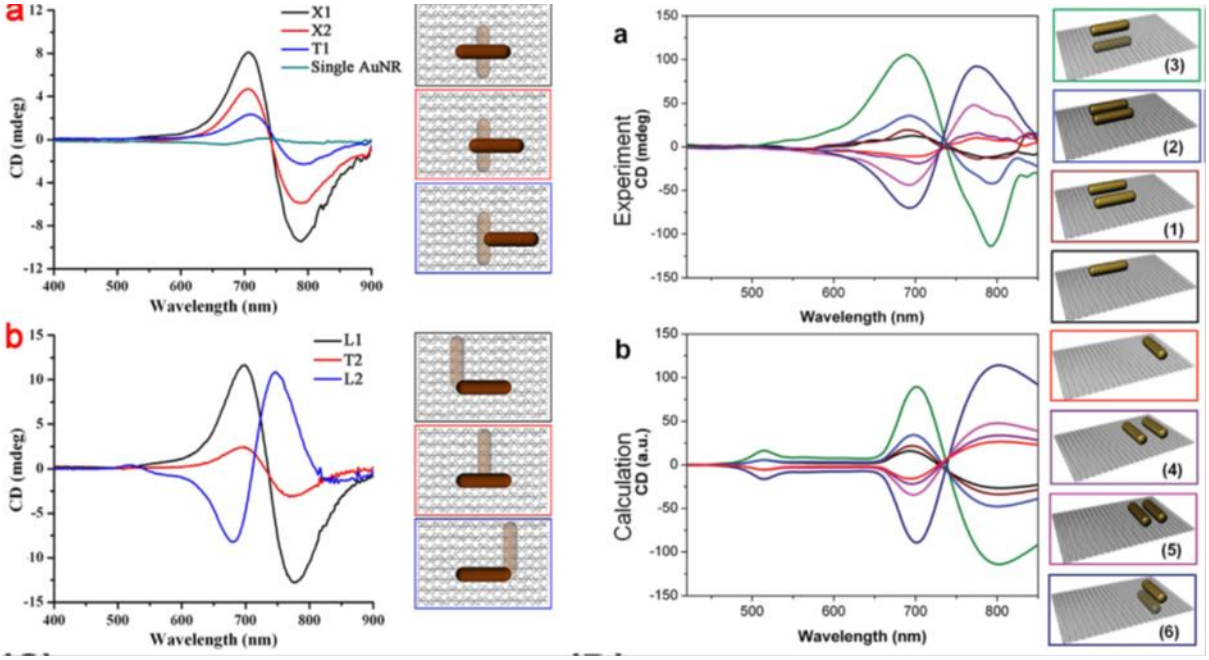


Fig 4. Representation of the orientation dependent chirality (reproduced with permission from ref. [20])

Template mediated chiral nanoparticle synthesis stands as an interdisciplinary area between supramolecular as well as nanochemistry. The primary approach of the work is to synthesize long supramolecular templates, which must be chiral. Then gold nanoparticles have been absorbed on the surface of the supramolecular template followed by de-templatization. The first challenge is to synthesize the perfect template or polymer with a chiral orientation. The second and vital challenge is to break or detach the templates without disturbing the nanoparticles' assembly. Thomas *et al.*, used D and L phenylalanine with a highly conjugated rigid hydrophobic moiety as a supramolecular template as the template is thermoresponsive, and breakable on mild heating.[22] Unlike the previously reported dimeric nanorod, they have just used thiolated spherical very small (4.5nm) gold nanoparticles reduced by $NaBH_4$ to absorb the supramolecular surfaces. The orientation of the absorbed gold nanoparticles in one isomeric template is entirely opposite of other isomeric template that leads to form completely oppositely oriented superstructures (enantiomeric superstructures) after removing the thermoresponsive templates.

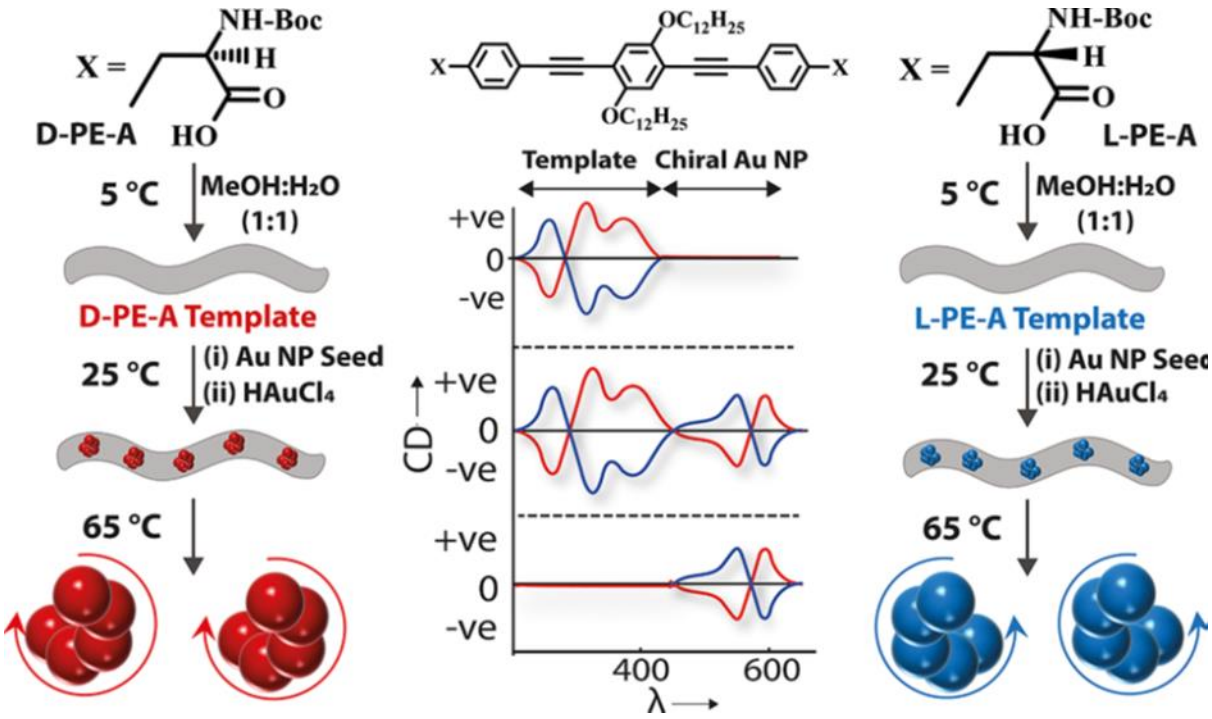


Fig 5. Thermo-responsive template based chirality. (reproduced with permission from ref. [22])

Again the researchers have used propellor-shaped large organic phenyl ring containing molecules for synthesizing the template. Several propeller-shaped molecules form helical supramolecular assemblies due to the pi stacking effect and hydrogen bonds. [23] The importance of the work is that synthesizing helical chiral gold superstructures without using DNA or any single helical unit.

Again they used porphyrin moiety, peptides, and different templates for synthesizing chiral superstructures.

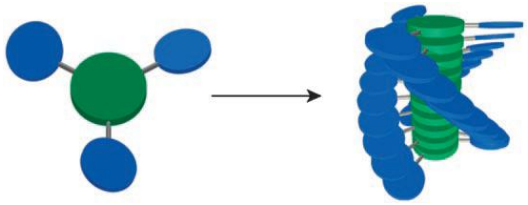


Fig 6. Representation of propeller shaped supramolecular framework (reproduced with permission from ref. [23])

Goldsmith and coworkers showed that chiral ligand-capped gold clusters could show optical activities. So the ligand-capped chirality basically has two perspectives to be discussed. The first one is just capping the ligand on the surface to show the chirality. Ulrich[24] and coworkers showed the chirality of D and L cysteine capped silver nanoparticles where the nanoparticles just absorbed the ligands on the surface area. Thomas Burgi[25] and coworkers used the BINAS ligand to stabilized the gold cluster having 11 gold atoms in a single cluster. Unlike the other cases, BINAS does not have any chirotopic center instead of a chiral axis. Besides this first approach, the second approach is to use the ligand to make self-assembly of nanoparticles. The difference between the linker and these ligands differentiates the concept from the previously discussed self-assembly approach. In the linker case, it helps to orient the nanostructures into some specific direction or form nanoarchitecture. However, here the ligands have a sufficient role in forming clusters themselves to introduce chirality. Chiral ligand capped gold nanorods are used in the core of nemetic achiral liquid crystals to make it proper chiral. In biosensing, there are massive applications of these ligand-capped chiral nanoparticles. Zhang et al.[26] showed the chiral sensing of cysteine enantiomers by using nucleotide capped gold nanoparticles. Zohr[27] and coworkers showed the chiral sensing of cysteine by using bacterial cellulose embedded silver nanoparticles. Zohr again used cellulose embedded gold nanoparticles to sense chiral alanine molecules in the lab in a syringe system.

Single Chiral Nanoparticle:

The above-discussed several aspects can introduce chirality and have massive applications, but they are either assemble or ligand embedded. Researchers have shown two simple gold nanorods' orientation effect to make chiral nanoarchitecture, but now the question is much bigger than it. Is it possible to make a single nanoparticle, not superstructure, chiral? Though there are several techniques like lithography to make a single nanoparticle chiral, it cannot be applicable for a large number of structures. So, the challenge is to synthesize large number of homogeneous chiral nanoparticles and their proper enantiomer.

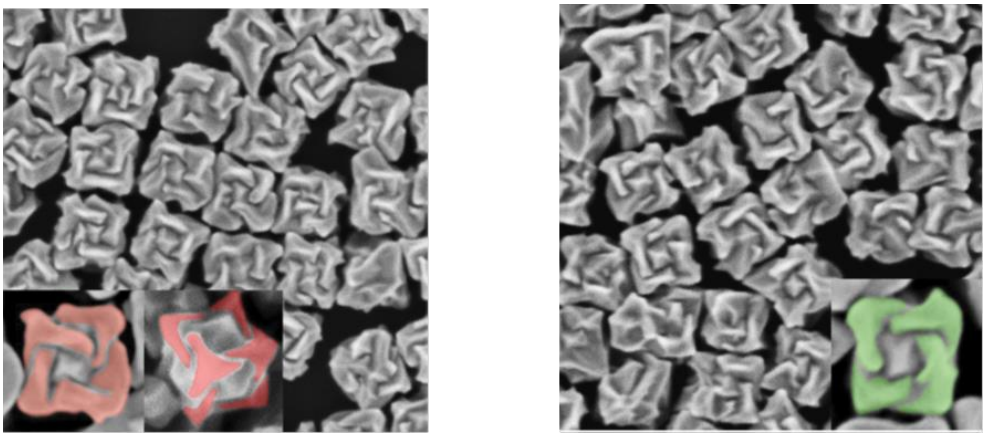


Fig 7. Enantiomers of single chiral nanoparticle (reproduced with permission from ref. [28])

In 2018, Prof. Ki Tae Naam et al. first reported the single chiral nanoparticle. Unlike the previous cases, his team focused on the inner morphology of nanoparticles. The synthesis process consists of two-step wherein the first step; the gold nanoseed are produced. In the second step, by using an optimized chiral growth solution, chiral nanoparticles are produced. Briefly, in the first step, the gold seed is formed from gold salt by $NaBH_4$ reduction. The seeds are usually spherical and having low index facets. These seeds are processed in a growth solution to change of low index facet to high index facets. The concept of the high index facet is the key of the whole research. Then, the thiolated chiral molecules are attached to the high index facets and shift the edge to change the shape to make it chiral. The first question lies in the utility of high index facets and their energy differences from low index facets. The geometry of facets decides the bond numbers between that facet and thiolated molecules. Usually, high index facets can form multiple bonds, whereas low index facets geometry does not allow making many bonds. Their studies have used D and L cysteine as chiral introduction agents and performed reactions following the concave cubic condition. The mechanism that they have established is that the distance of the amine group and thiol group determines the shifting of boundaries leads to change in the growth rates on the two sides. Thus the chirality was induced in single nanoparticles. They performed controlled experiments by using BOC-protected amino acids, but no chirality was observed. That raises another question regarding the interaction between the amine group of cysteine and gold facets.

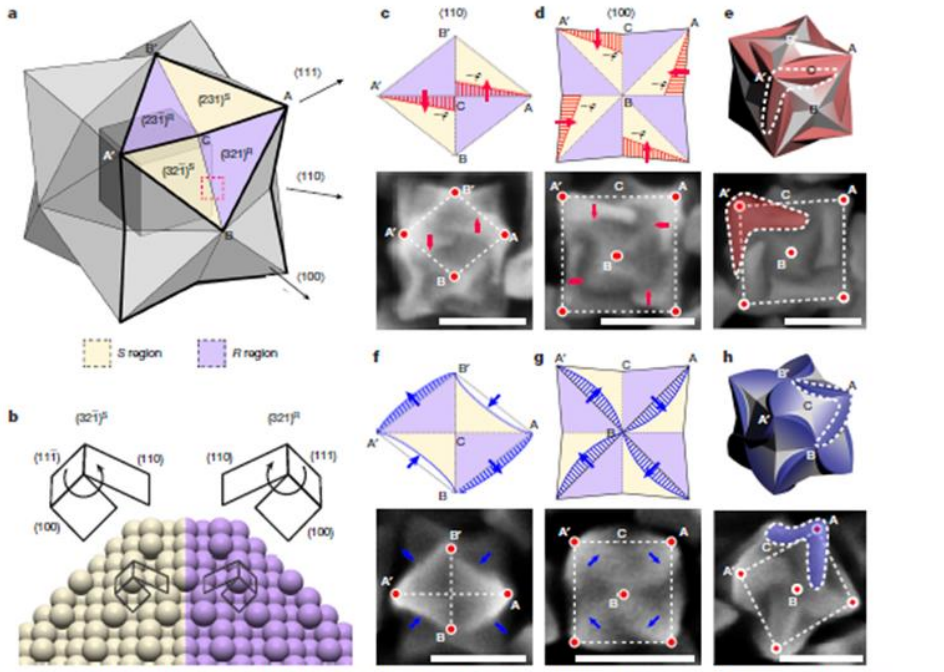


Fig. 2 | Mechanism of chirality evolution through the interplay between the enantioselective binding of molecules and the asymmetric growth of high-index facets. a, Schematic of a stellated octahedron, differentiated by high-index facets consisting of $\{321\}^S$, (*S* region, yellow) and $\{321\}^R$ (*R* region, purple) configurations. The vertices of the [111], [100] and [110] directions are indicated as A, B and C, respectively; A′ and B′ refer to the symmetric points of A and B, respectively. **b**, Comparison of the atomic arrangement of the $(321)^R$ and $(321)^S$ gold surfaces for region indicated by the red dotted box in **a**. The conformation at 'kink' sites is defined by the rotational direction of low-index microfacets in the sequence (111) → (100) → (110): clockwise, *R* region; anticlockwise, *S* region. **c**, **d**, Schematics (top) and SEM images (bottom) of *R*–*S* pairs showing the morphological development of 432 helicoid I in the presence of L-Cys, as viewed along the [110] (**c**) and [100] (**d**) directions. Newly developed boundaries are indicated as red patterned areas with arrows; each vertex is marked on the corresponding SEM image. **e**, Three-dimensional model (top) and SEM image (bottom) of the final chiral shape. The newly formed *R* region is coloured red and the chiral element is indicated by the dashed outline. The red shaded region in **e** is equivalent to the red patterned areas in **c** and **d**. **f**, **g**, Morphological development of 432 helicoid II in the presence of L-GSH. **h**, The corresponding final chiral shape. The newly formed boundaries and the pinwheel-like chiral elements of the final shape are coloured blue. Scale bars, 100 nm.

Fig 8. Schematic representation of the morphological development of chiral nanoparticles (reproduced with permission from ref. [28])

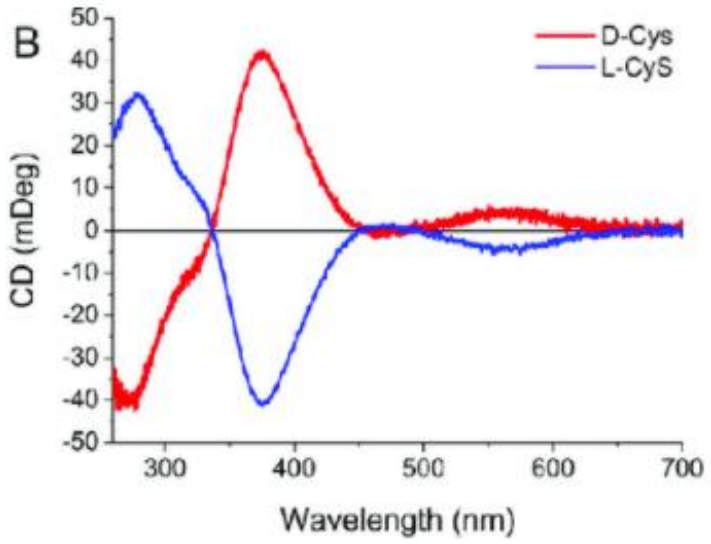


Fig 9. CD spectra of the enantiomers of the chiral nanoparticles (reproduced with permission from ref. [28])

Besides the cysteine, they have used glutathione as well as some peptides to observe the differences of chirality in different cases. They observed the different structures as well as different chiral responses from the particles. The absorption UV spectra are identical for both enantiomers as per expectation, and CD spectra are entirely reversed and different from amino acids or peptides. After the reactions, the capped amino acids can be removed by using NaBH4.

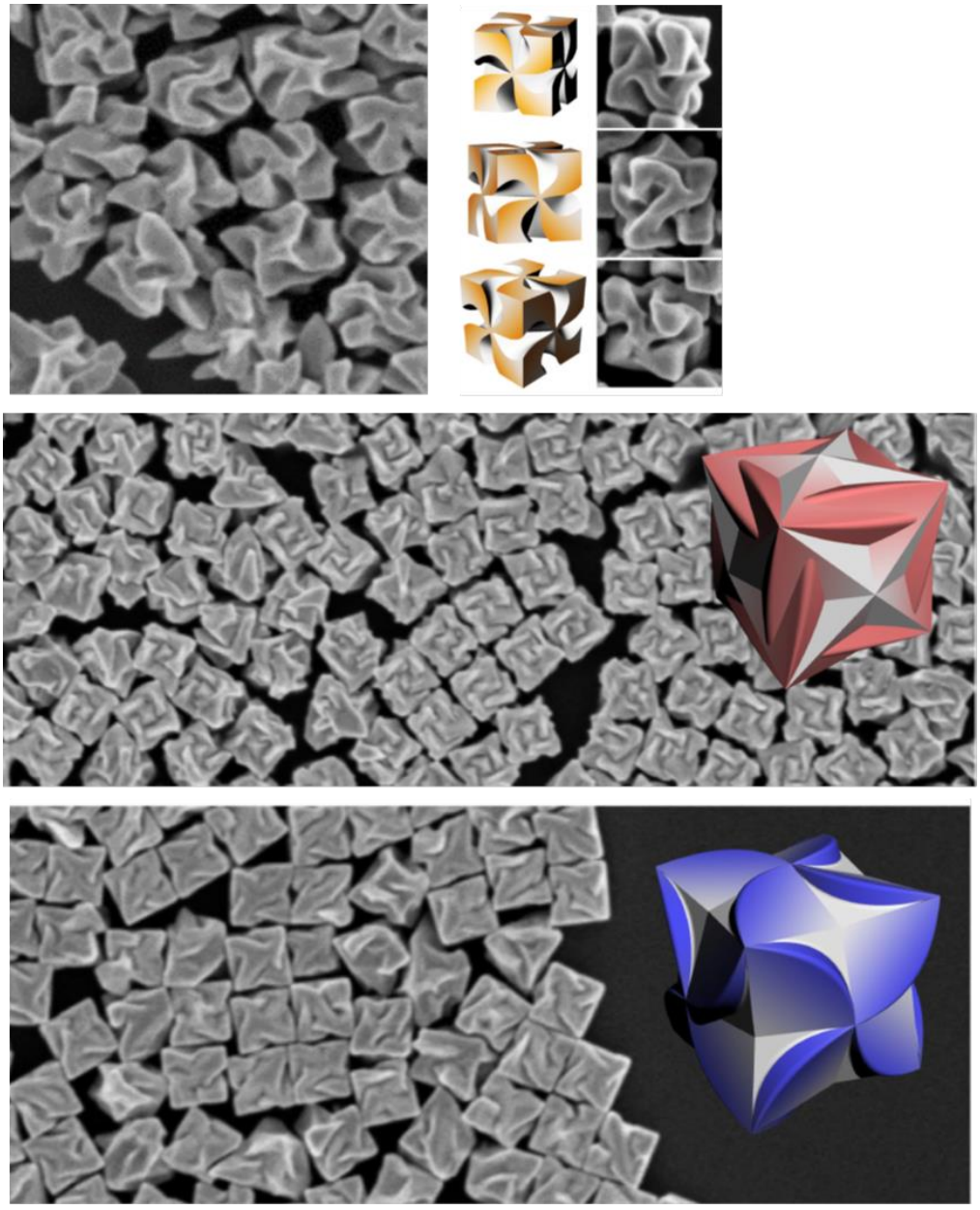


Fig 10. Different chiral nanoparticles by using different peptides and amino acids. (reproduced with permission from ref. [28])

These shapes are highly optimized. Without visualizing CD spectra, chirality can be confirmed by SEM images as the beautiful images of orientations are present. Before and after the optimization limit, there must be some chirality, but that cannot be predicted without CD. A very little difference in amino acid volume can totally change the shape of the nanocrystals. Wulf's polyhedron is formed at the early stage of the reaction, and the edges of polyhedrons are tilted and shifted differently for different amino acids. If the amount of amino acids exceeds the optimization limit, there will be overgrowth, making the structure complicated. Time plays a significant role here as it takes only two hours to be formed, and before the optimized time, the reaction doesn't show any proper shape, but the shifting of edges has adequately started after 20 minutes. The excess time can also deform the structures.

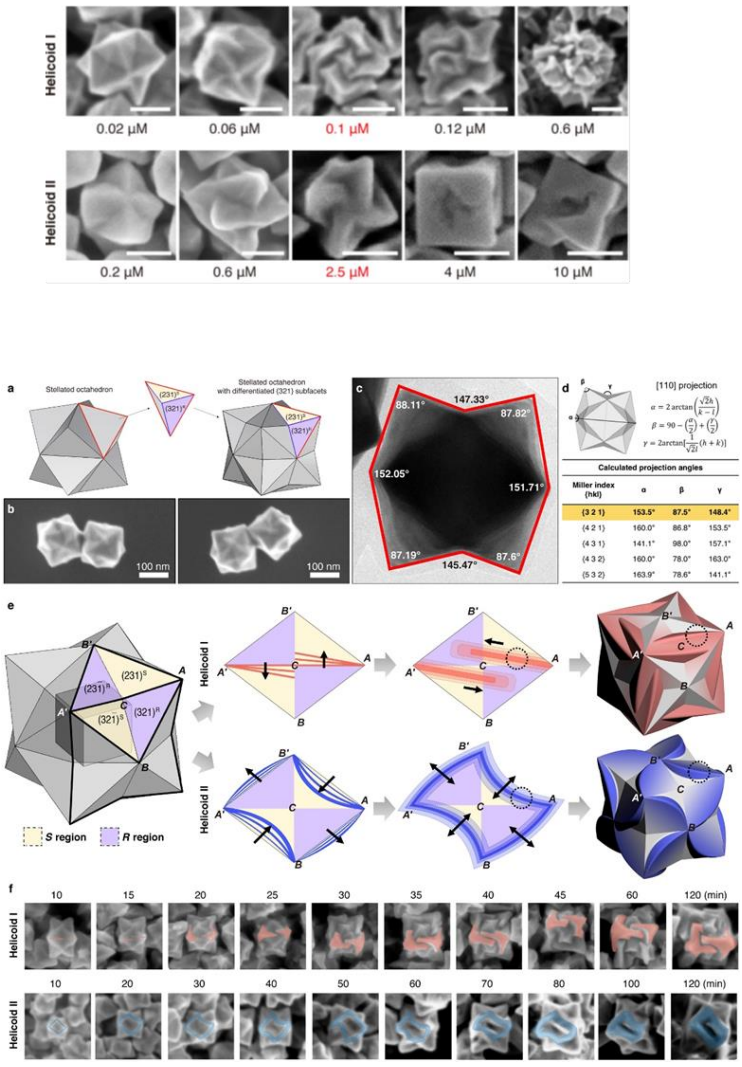


Fig 11. Schematic representation of mechanism and optimization limit of the reaction (reproduced with permission from ref. [28])

Motivation of the Work:

We believe chiral sensing is one of the most significant topics in academia as well as the industrial sector. At 1960, the time of 'Phthalimide Disaster', the community understood the necessity to work on the chirality. Research labs need highly sophisticated instruments like CD, HPLC, Polarimeter, etc. Several small laboratories and industries do not afford these types of costly instruments, and in industries, use of these instruments makes the cost of products too high. Just imagine, if the chirality of compounds can be detected by only using a UV spectrometer, then the chemistry will be much easier for the research purposes.

Nanoparticles can absorb or can cap several types of ligands, amino acids, proteins, and other molecules to show a high shift in UV-Visible spectra. If chiral nanoparticles can absorb the selective enantiomer of the analyte and show maxima shift in UV Visible spectra, it can be very much impactful for the science community.

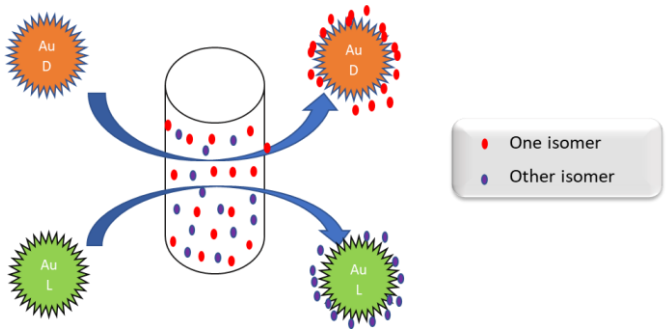


Fig 12. Schematic diagram of the proposed idea of chiral sensing

Besides sensing, nanoparticles have massive utilities in the catalysis field. The chiral nanoparticles may have the potential to use as enantioselective catalysts.

In case of SERS, our expectation is adsorptions may be enantioselective on the chiral nanoparticle surfaces leads to different responses on different enantiomers. Our first motive is to check the SERS effect using any enantiopure analytes on the same chiral enantiomeric nanoparticles. As per the primary expectation, one enantiomer shows SERS enhancement, whereas the other may not respond in SERS. Below, the image of SERS spectra was given to understand the amplification of the intensity.

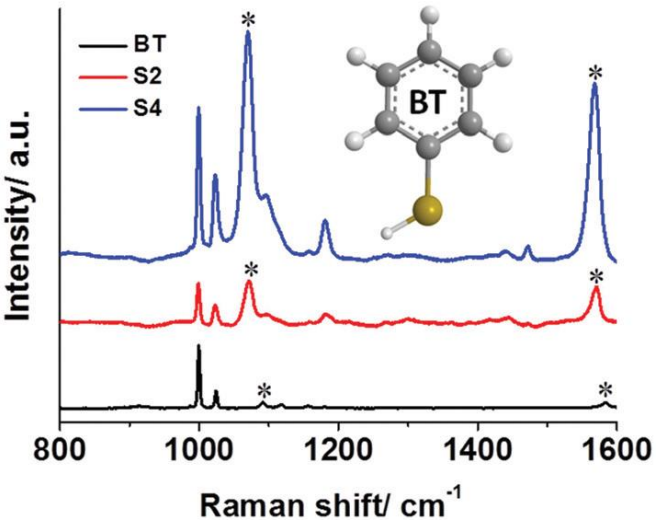


Fig 13. The SERS spectra of BT (reproduced from 29)

Goal of the Project:

The preliminary target is to develop different chiral nanoparticles by following the same procedure by Ki Tae Nam. The key factor of his work is the high index facet, on which the thiolated amino acids are attached and shifting the edge boundary to introduce chirality. In his work, he used low index facet nano seed, and it was converted into high index facets in the growth solution, and then amino acids approach the facets.

In our scheme, we have chosen the nanostructures which have high index facets instead of nano seeds. The reaction contains three steps where in the first step, the gold nano seed has been synthesized. Then following proper protocols, high index facets gold nanostructures like concave cube and tetrahexahedron were synthesized. In the last step, that high index facet containing nanostructures was treated with a chiral growth solution. The concave cube has 24 high index [720] facets, and we have selected it for making chiral nanoparticles.

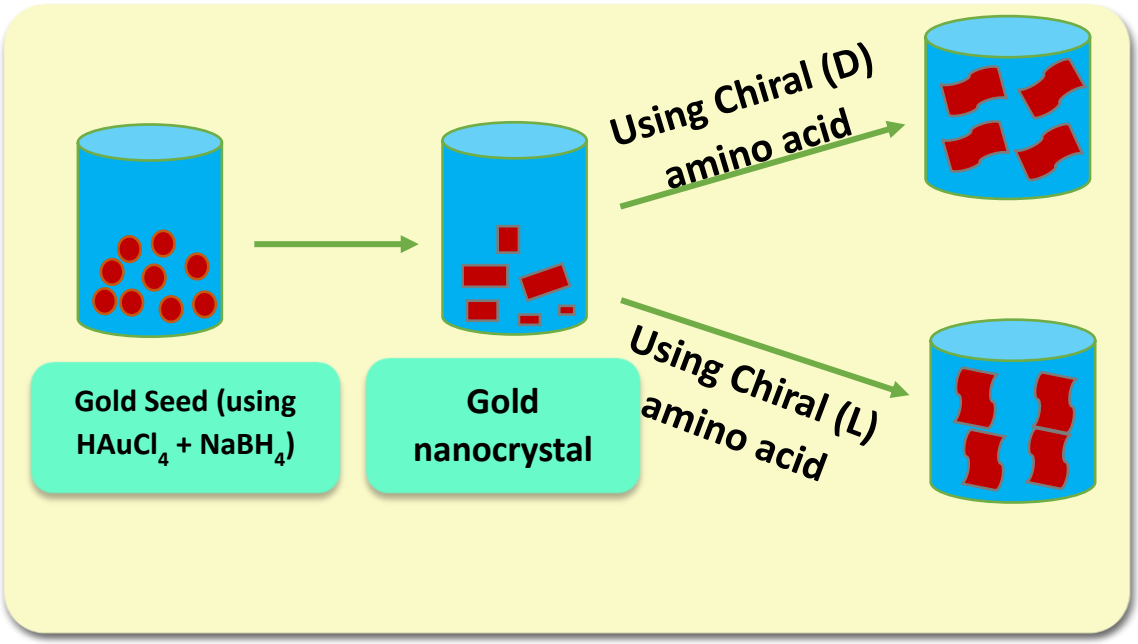


Fig14. Schematic diagram of strategy-1

Besides the Concave cube, the elongated tetrahexahedron has high index facets [730]. As the elongated tetrahexahedron size is much bigger than the small concave cube, we have planned to add chiral amino acids in the second step (strategy-2). Briefly, the scheme is to take any standard established protocol of the synthesis of tetrahexahedron and add

chiral thiolated amino acid. The amino acid attachment on the gold surface is reversible. If amino acid attaches on the low index facets when the reaction is just initiated, gradually, it attaches on the high index facets and detaches from the low index facets due to higher stabilization.

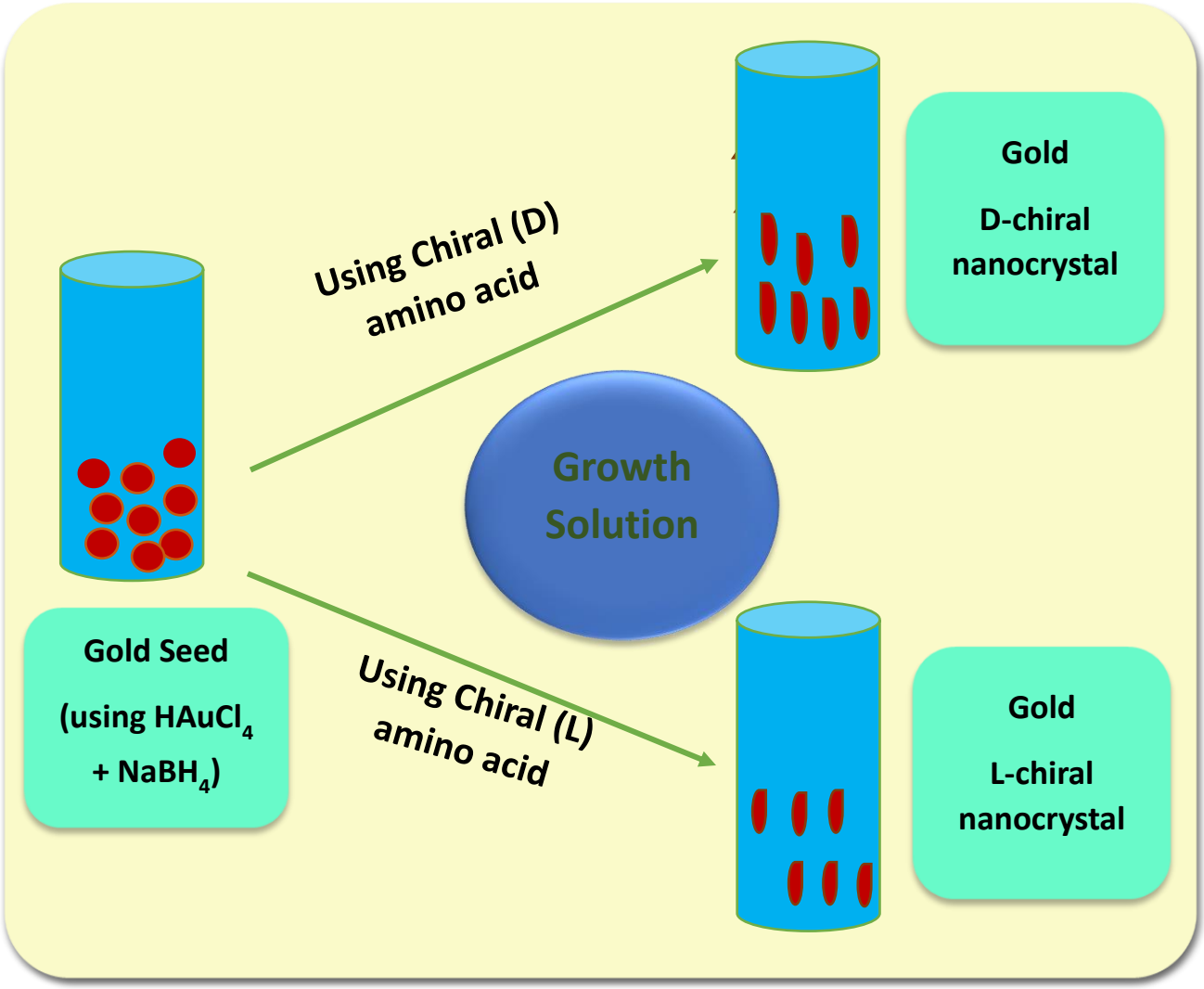


Fig 15. Schematic diagram of strategy-2

This scheme was also performed with concave cube where the chiral acids were added in the growth solution of the concave cubes to observe the chirality.

Experimental Section:

Chemicals-

Cetyltrimethylammonium chloride (CTAC), cetyltrimethylammonium bromide (CTAB), Chloroauric acid ($HAuCl_4$), Sodium borohydride ($NaBH_4$), Tannic acid, D-Cysteine hydrochloride, L-cysteine hydrochloride were purchased from Sigma-Aldrich and Silver Nitrate ($AgNO_3$), Hydrochloric acid (HCl), Ascorbic acid were purchased from SRl. 99.9% pure Acetone and Millipore water.

Methods:

Strategy-1

Synthesis of Gold Concave Cube Seed:

All glassware, magnetic beads, measuring cylinder were washed with aqua-regia solution and soap solution. 320 mg of CTAC was taken on a 30ml glass container, and 10 ml of Millipore water was added to prepare 100mM CTAC solution. 3.7mg of NaBH4 was taken in a small microcentrifuge tube, and 1 ml of Millipore water is added to prepare 100mM solution, followed by ten times dilution to 10 mM. The NaBH4- solution was placed in the deep freezer to make it ice cold. The 10 ml CTAC solution was stirred on the magnetic stirrer, and 0.25 ml of 10mM gold solution was added. Then 0.60 ml of NaBH4 solution was added to change the color of the solution from yellowish to light brown.

Synthesis of Gold Concave Cube:

The growth solution was prepared following Chad Mirkin's[36] pathway by consecutively adding 0.50 mL of HAuCl4 (10 mM), 0.10 mL of AgNO3 (10 mM), 0.20 ml HCl (1.0

M), 10 ml CTAC (100 mM). The color of the solution was turned to pale yellow, and then 0.10 ml of 100 mM Ascorbic acid was added to make the solution colorless. The previously prepared gold nano seed was diluted ten times, and 0.10 ml was added to the reaction mixture under the stirring condition. The solution was incubated for 12 hours without creating any mechanical disturbances.

Three-step Approach to the Synthesis of Chiral Gold Concave Cube:

The solution of the gold concave cube was centrifuged and washed with pure water, and was redissolved in water. The growth solution was prepared by consecutively adding 0.25 ml of HAuCl4 (10 mM), 0.05 ml of AgNO-3 (10 mM), 5 ml of CTAC (100 mM), 0.05 ml of 100mM ascorbic acid. The 0.05 ml of the redissolved concave cube was added to the reaction mixture under the stirring condition. After 10 minutes, 0.1 ml of 10 micromolar chiral cysteine solution was added, and the solution was kept for three hours.

Strategy-2

Two-step approach to synthesis of chiral nanoparticles from Concave cube seed-

Consecutively adding all reagents as described in the ‘synthesis of gold concave cube’ section. After successfully adding all, 100 mM 10 µl chiral Cysteine solution was added to the solution. After 12 hours of the reaction, the solutions were subjected to the workup.

Synthesis of Gold Tetrahexahedron Nano Seed[29]-

364.4 mg of CTAB was taken in a clean vial, and 5 ml of Millipore water was added to prepare a 200 mM solution. 7.4 mg of NaBH4 was dissolved in 1 ml Millipore water to make 20 mM solution and was kept in a deep freezer to make it ice cold. In a clean

beaker, 1 ml of Millipore water, 1.25 ml of CTAB, and 0.156 ml of 4 mM $HAuCl_4$ were added. Then 0.075 ml of $NaBH_4$ was added to the solution under stirring, the color of the solution was changed to deep brown. The solution was kept for a minimum of one hour.

Synthesis of Chiral Gold Tetrahexahedron-

In a clean vial, 1 ml of 200 mM CTAB solution was taken. 0.02 ml of 0.1 M NaOH, 0.25 ml of $HAuCl_4$, 0.03 ml of $AgNO_3$ were added consecutively. The color of the solution became pale yellow, and then 0.69 ml of pure water was added to make up the volume. 100 mM solution of tannic acid was prepared, and 0.01 ml of it was added to the solution. Unlike the other case, the solution turned into less bright yellowish. After 10 minutes, 0.01 ml of previously prepared seed solution was added. One hour after adding the seed solution, the 0.1 ml of 10 mM of chiral cysteine was added to it under the stirring condition. The solution was incubated for 12 hours.

Work Up Process-

After the reaction of each, there are several impurities, surfactants, amino acids, reducing agents in the solution. To clean up these impurities, the reaction mixture was taken in small plastic mcts and were centrifuged for 4 times under 9000 speed for 10 minutes each. Supernatant liquids were taken out and vials were filled up with Millipore water and acetone.

Characterizations:

UV-Visible Spectroscopy-

UV- Visible spectra of the aqueous solutions were measured using Cary 5000 UV-Vis NIR (Agilent Technologies) spectrophotometer at the scan rate of 1 nm/s. Quartz Cuvette of 1 cm path length was used for recording the spectra at room temperature. Each time baseline correction had been done for every solvent, to eliminate the effect of solvents on spectra.

Transmission Electron Spectroscopy (TEM)-

Transmission electron microscopy (TEM) studies were pursued using JEOL model JEM-F200 equipped with energy dispersive X-ray scattering facility (EDS). The sample was prepared by drop casting 0.02 ml of the suspension on the carbon coted Cu grid, followed by heated in oven and was treated under high vacuum.

Field Emission Scanning Electron Microscopy (FESEM)-

Field Emission Scanning Microscopy was carried out by using JEOL-7600F. The samples were prepared by drop casting of the sample solution on the small piece of silicon wafers. After drop casting, these silicon wafers were dried in the hot air oven and then placed in a high vacuum desiccator.

Circular Dichroism (CD) Spectroscopy-

The CD spectra had been taken by using Chirascan CD Spectrometer. The sample was diluted in water to keep the High Tension value lower. The solution was well sonicated before taking the spectra.

Results & Discussions:

Although several research pieces have been done on template-mediated or ligand-mediated chirality of particles, it is still very challenging to produce single chiral nanoparticles. The concept of single chiral nanoparticles came in 2018, and there are several aspects to be discovered. The fundamental concept of chirality lies in the interaction between high index facets and thiol-containing amino acids. Unlike using high facet nano seed, We prefer to use high-index facets containing nanoparticles as seeds to introduce chirality. The work has not been finished yet, and there are several characterizations that should be done to ensure chirality.

Our basic focus was to establish a protocol where the homogeneously shaped nanoparticles would be formed. The Scheme was divided into three major types of research. The first one is the synthesis of a large number of homogeneous nanocrystals. The synthesis of perfect shape nanocrystal is still challenging as disturbing the specific ratio of the gold solution and reducing agent leads to produce different types of nanocrystals with different shapes and sizes. The detailed chemistry behind the shape and sizes of nanoparticles was discussed in the next project. The second aspect of the project is to ensure the chirality by CD spectra if it cannot be detected by following the shapes. The challenge is to determine and optimize the concentration of specific amino acids or peptides. The optimization limit is different for different amino acids, and in particular amino acid volume and concentration, the particles may show the highest and observable CD spectra value. The last aspect to show the applications of these chiral nanoparticles on chiral sensing.

I have synthesized and reproduced the same homogeneous stone-like structures with very rough and asymmetric surfaces in this work with the concave cube, which was detected by FESEM. The question lies if this rough asymmetry is limited on the surface or it is inside the nanostructure. Does the most important question arise if this asymmetry makes the nanoparticle chiral or not? To answer the queries, we need to check the CD spectra. Unfortunately, the CD spectra at our institute has stopped working, and in this Covid-19 situation, we could not avail it from other institutes.

Earlier the using concave cube as seed, we have performed the two-step experiment, as described above, with tetrahexahedron and D-cysteine hydrochloride. There was a

continuous peak from the negative to the positive side near about 350 nm. However, the shape and the sizes were not homogeneous. To make the process purely reproducible, it is very much essential to bring perfect homogeneous structures.

Synthesis of Concave Cube-

By following the protocol, the gold concave nanocubes were synthesized. The whole reaction has been performed in the CTAC medium as CTAC has a vital role in this synthesis. Capping agents cap the particular facets to make them grow in a perfect pattern. Here, CTAC, especially chloride, controls the selectivity towards the concave cube. One of the researchers' team[48] performed the same reaction by using CTAB instead of CTAC, and they found tetrahexahedron instead of concave cubes.

In the synthesis of gold nanostructures, silver salt has an important role also. They are used as the sacrificial metal. Reducing agents reduce some portions of silver before the reduction of some portions of gold. The shape of the particles depends on the reduction rate of the metal, and sacrificial metals help to control the reduction rate.

Hydrochloric acid was used to control the acidic pH.

Ascorbic acid was used as a reducing agent. In the case of seed preparation, $NaBH_4$ was used to reduce Au^{3+} ion to Au^0, but here ascorbic acid reduces Au^{3+} to Au^+ ion. The color of the solution was changed from yellowish to colorless. The ratio of the gold salt and ascorbic acid has the highest control on the shape determination.

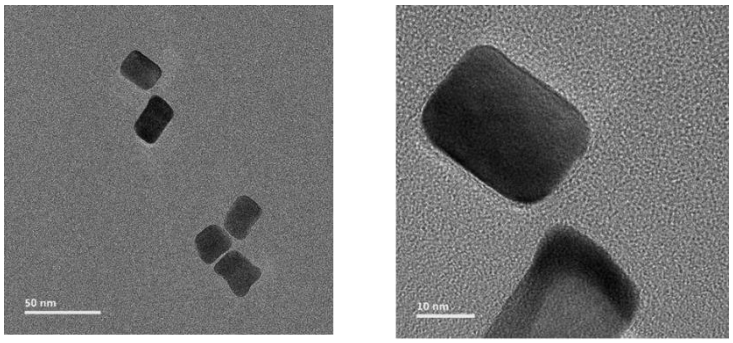


Fig 16. TEM images of Concave Cubes

As this was used as a seed for the next step, the size of the particles were small. There's a beautiful concept of size optimization by diluting the seed solution. According to the

protocol, seeds are diluted from 10 times to 100000 times to get the preferable size. The process of nanoparticle formation has started just after the addition of the seed. The reduced Au^{+} ion approaches the seed, and it changes to bigger particles. If the conditions are the same, which means the concentrations of Au^{+} ions are the same, then adding the small number of seeds leads to produce bigger nanostructures, and the higher number of seeds leads to produce smaller nanostructures. Here, the seed solution is diluted ten times to get small nano concave cubes.

Three-step Approach to the Synthesis of Chiral Nano Concave Cube (Startegy-1)-

In the experiment, gold concave nanocubes were taken as seeds and treated with growth solutions containing chiral cysteine. There are no such colorimetric changes while the products were formed. After three hours, the nanoparticles precipitated at the bottom of the container, indicating the end of the reaction.

The products were looking like stones having some specific architectures, and some of the architectures were so pronounced that the particles were looked like nanoflowers with petals. The shape of these nanoparticles is extremely homogeneous, and the size is about 200 to 250 nanometer.

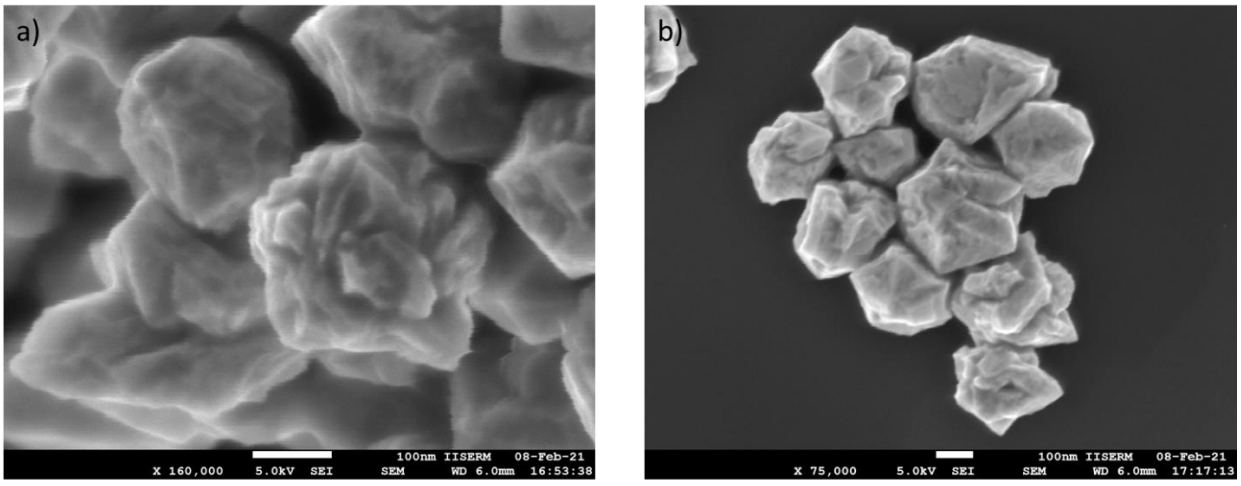


Fig 17. FESEM images of products

Besides the product, some clear polyhedral structures are observed, and in several non-polyhedral particles, the facets and edges of polyhedral are observed. According to the Wulf Polyhedral theory, the nano seeds are formed very small (2 to 4 nm) polyhedral (spherical polyhedral) structures, and then the capping agents or chemicals promote one of the facets over others. However, the polyhedral's size is similar to the nanoparticles (about 200 nm). We have detected the polyhedral where the bottom side was changing to form some shapes, but the upper side was intact. This type of polyhedral may carry information about the reaction mechanism. The Silicon wafers were partially damaged, so background of the FESEM images are not clear.

There are only two possible explanations of the presence of polyhedral structures. Either it is the side product though it is very less in number, or is the intermediate.

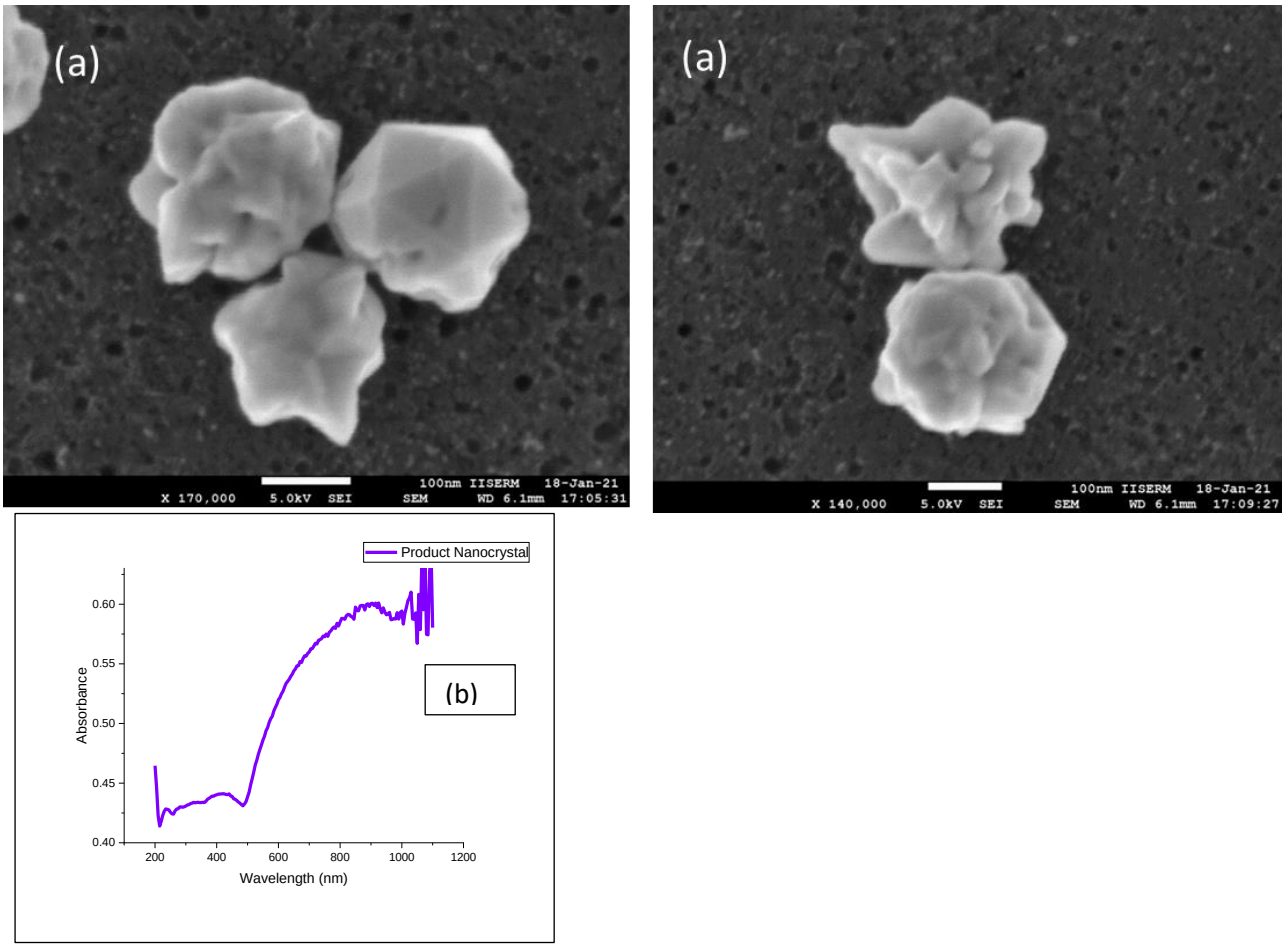


Fig 18. a) FESEM images of the presence of etched polyhedron b) UV-Visible Spectra of the product nanocrystal

Time Optimization Studies-

Ki Tae Nam and his team got some haphazard shapes of their chiral nanoparticles until they succeed on their optimization. In most of the cases, the concept of time optimization are used to increase the yield of the product but in case of chirality by the minute time optimization perfect shapes can be detected. Another aspect of the time optimization studies is to answer the question on the presence of the polyhedral structures.

After the time optimization from 2 hours to 6 six hours, it was observed that the structures remained approximately same from 3 hours to 6 hours. The structures got in 2 hours, having more polyhedral facets and less ‘architecture’ indicating the reaction pathway and the formation of polyhedral structures as intermediate.

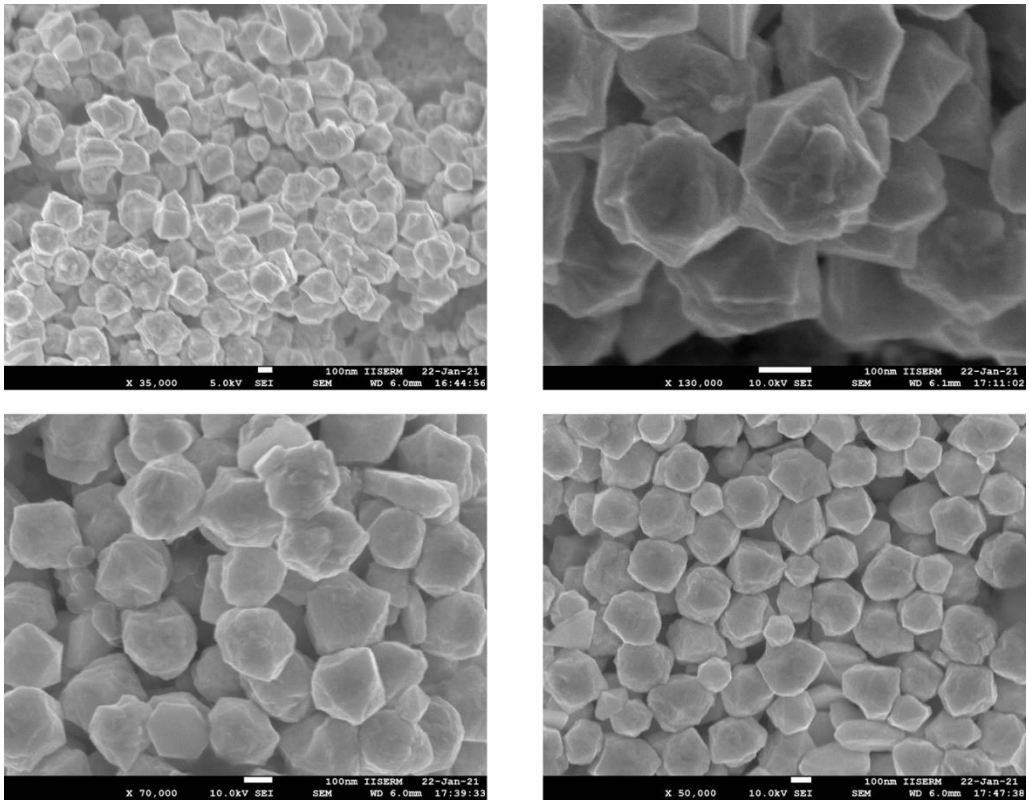


Fig 19. FESEM images of product after 2 hours

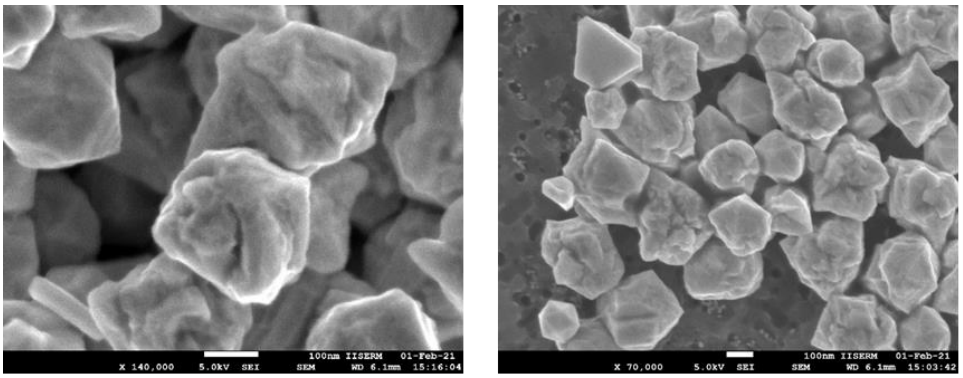


Fig 20. FESEM images of product after 3 hours

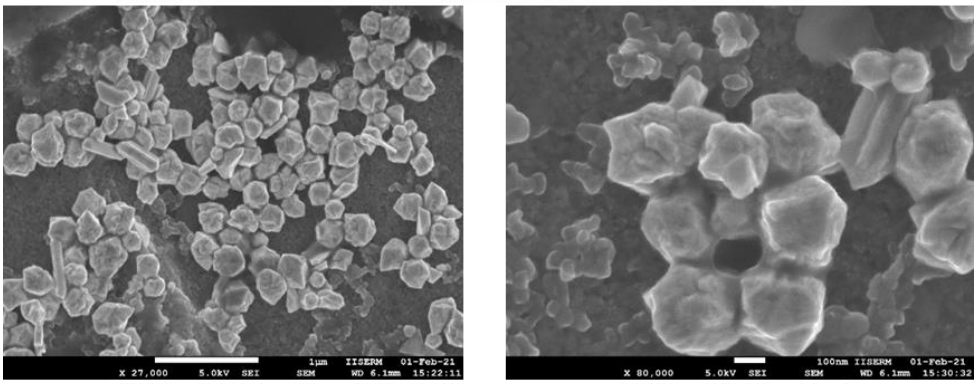


Fig 21. FESEM images of product after 4 hours

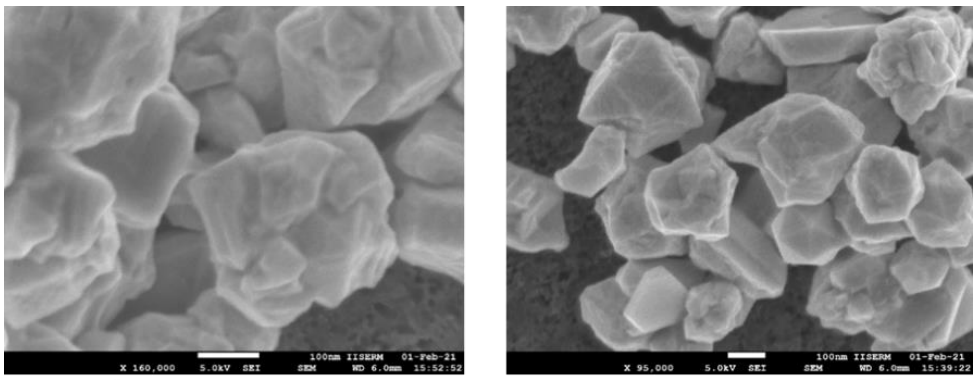


Fig 22. FESEM images of product after 5 hours

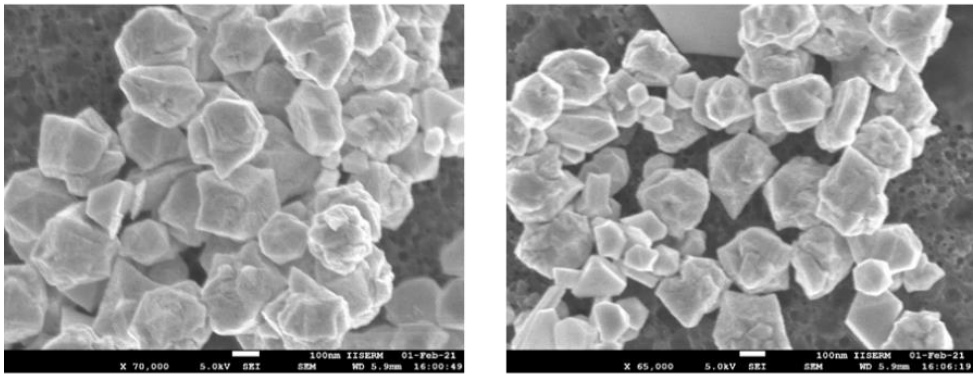


Fig 23. FESEM images of product after 6 hours

Concentration Optimization Studies-

The amino acids can change the reduction potential as well as the shape of the particles without introducing chirality. So, it is crucial to optimize the concentration as well as volume. Higher concentrations of the amino acid can make overgrowth of the particles and make the surface smooth. We have varied the concentration from 7.5 millimolar to 7.5 micromolar to observe the effect of the concentration on the shapes. At 7.5 millimolar, the shapes are random and do not have any helical or any bend. Though TEM is not enough to observe the surface architectures at lower concentration like 75 micromolar or 7.5 micromolar, the change in structures were observed. At 7.5 micromolar concentration the better structure was observed than other concentrations, so 10 micromolar concentration of cysteine was fixed as the optimal concentration.

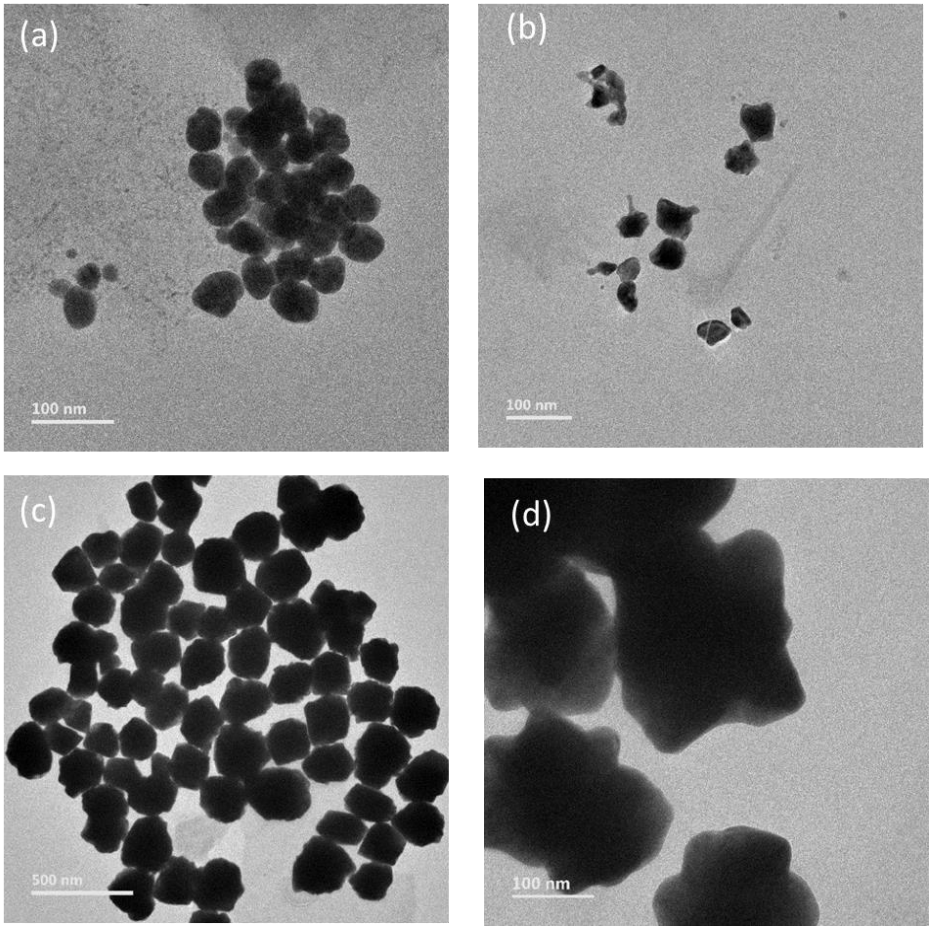


Fig 24. TEM images of the products with different concentrations of amino acid. a) 7.5 mM of D-Cysteine b) 0.75 mM of D-Cysteine c) 75 micro molar of D-Cysteine d) 7.5 micro molar of D-Cysteine.

Volume Optimization Studies-

Prof. Ki Tae Nam and his team have shown that the nanoparticles' chirality and shape have changed with the volume of the amino acids. The volume optimization studies was performed to observe the changing of shapes with volume. Though the structural changes were observed with changing the concentration, in the case of volume optimization, no structural changes were defined.

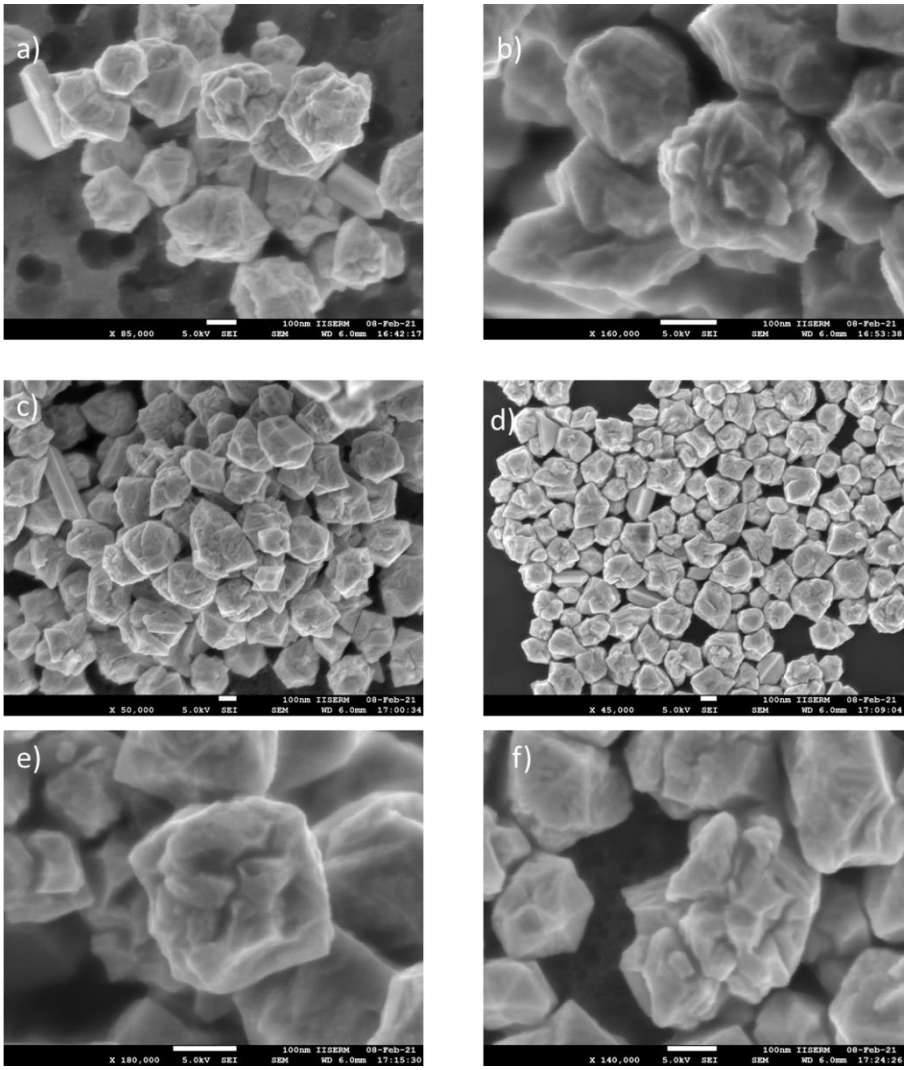


Fig 25. FESEM images of the products with different volumes of amino acid- a) 20 b) 40 c) 60 d) 80 e) 90 f) 100 microliters.

Controlled Experiment and Conclusion-

The controlled experiment arises question on the entire project, as we observed that the same structures were formed without the presence of any amino acid.

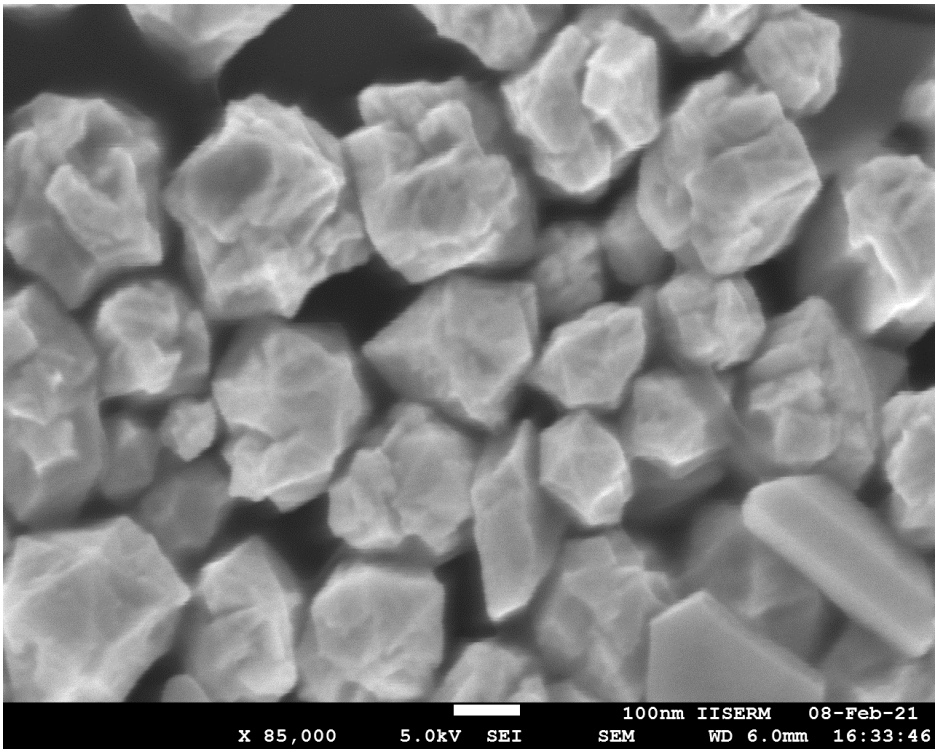


Fig 26. FESEM images of the products without adding any amino acid

If these structures can be formed without the presence of any amino acids, then there should be no chirality in those particles. Hence the trial can be unsuccessful. However, there is another aspect: if any type of chirality present in the particles, then it is possible that shape may not indicate it. So the only way to know the chirality is to observe CD spectra.

The project is challenging and needed to be chirally optimized. My goal is to synthesize a large number of homogeneous particles, which will show chirality. The samples will be sent for CD spectroscopy as soon as possible, and then we will have any proper conclusion. All of the optimization experiment has been done using D-Cysteine.

Two-step Approach to Synthesis of Chiral Nanoparticles from Concave Cube Seed (Strategy-2)-

Following the second scheme by adding 100 microliters 10 micromolar amino acids in the same growth solution of the concave cube, we have tried to synthesis chiral nanoparticles. The idea behind the approach is the selectivity of thiolated amino acids on high index facets than low index facets. We have expected that at the early stage of the reaction, the amino acids attach on the low index facets of the seed, and gradually, as the high index facets generate, the amino acids shifts from low index facets to the high index facets and then the growth may have happened accordingly.

Here the NaBH4 reduced seed solution was diluted 100 times in desire to get big nanoparticles. But unfortunately, the size of the nanoparticles was small, and no rough or patterned surfaces were observed under FESEM.

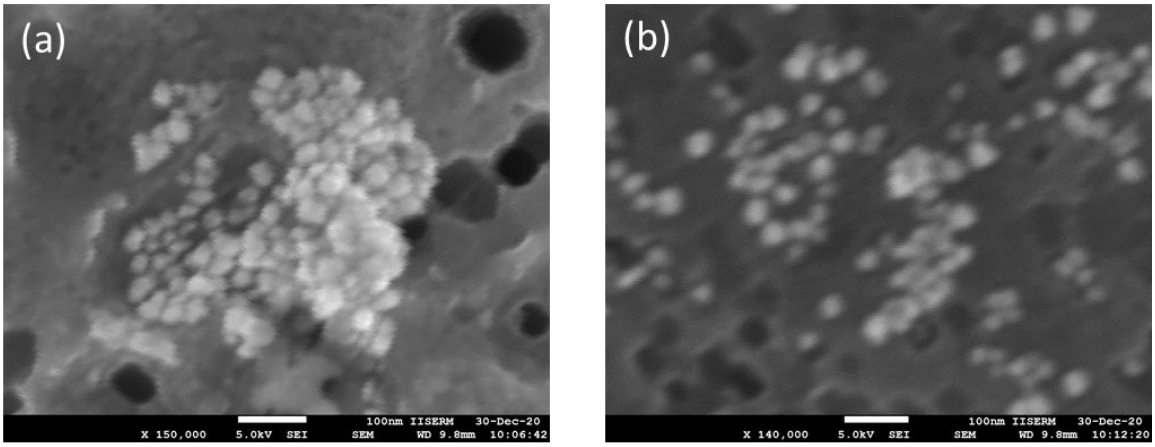


Fig 27. FESEM images of Products by following Strategy – 2 a) D- Cysteine b) L-Cysteine

Future Aspects-

In this synthesis, the amino acid was added at the beginning of the reaction. If it may the cause of the small size particles then time dependent addition can be performed in future. To need to understand the structure and surface design, high resolution FESEM is needed.

Two-step Approach to Synthesis of Chiral Nanoparticles from Tetrahexahedron Seed (Strategy-2)

The Same as the procedure for concave cube, the 100 microliters 10 micromolar D-Cysteine was added to the growth solution of the tetrahexahedron. We have followed the procedure established by Ballav et al., where they have used tannic acid for reducing agent to make the process environment friendly following the green chemistry route. Unlike the case of ascorbic acid, tannic acid makes the color of the solution deep yellow.

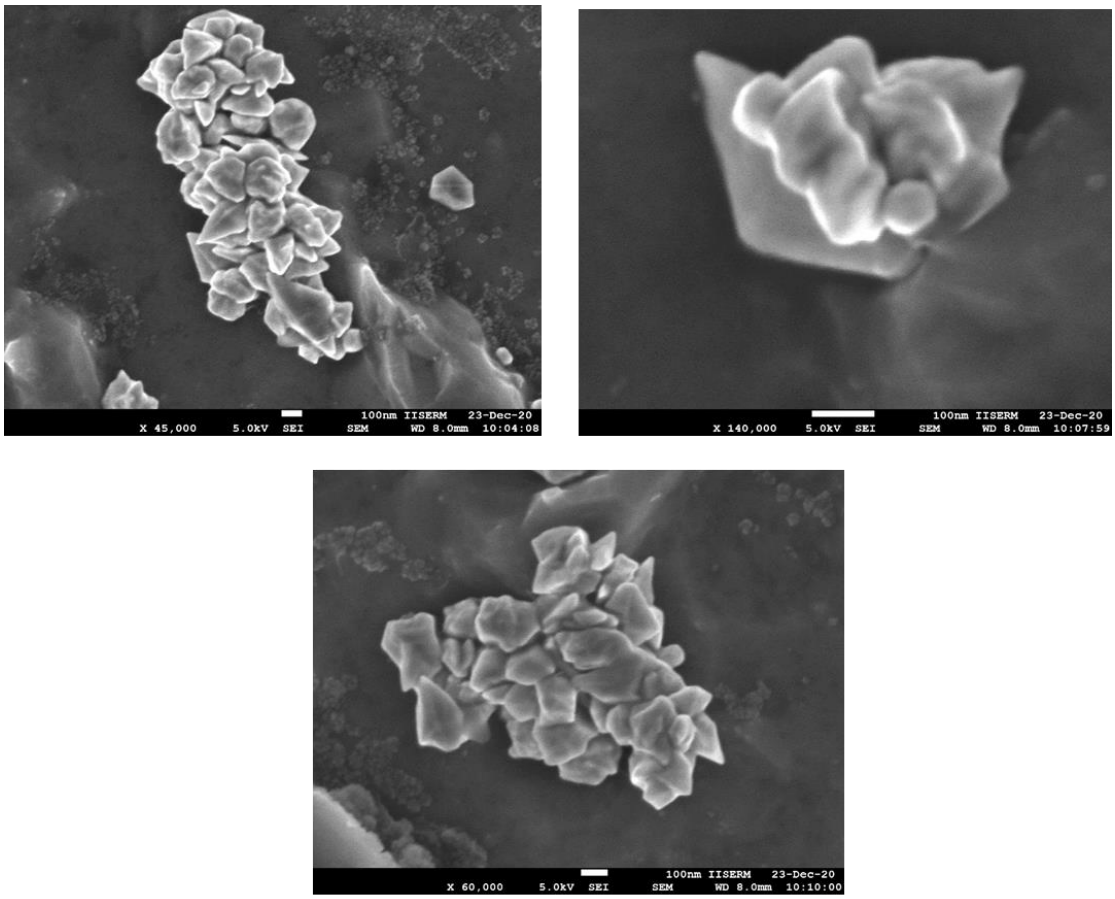


Fig 28. FESEM images of THH products by following strategy-2, using L-Cysteine

The products have sharp edges and the surfaces are rough and have some architectures. The size of the particles are near about 200 nm though all particles aren't same in size. The synthetic pathway should be developed to produce a large number of homogeneous particles of same shapes and sizes.

It has a sharp peak at near 400 nm at CD spectroscopy which indicates the development of chirality in the particles.

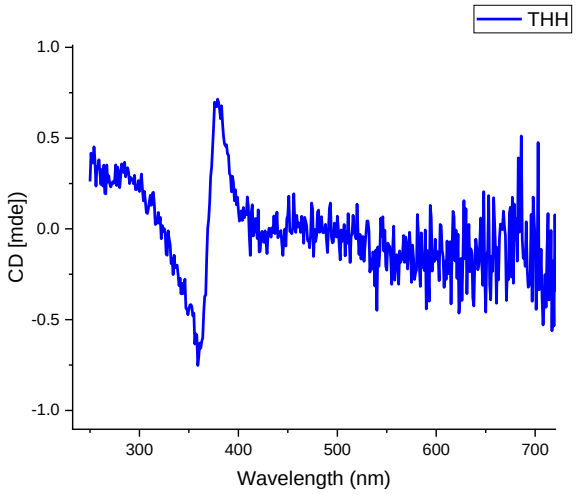


Figure 29. CD spectra for the tetrahexahedron product by following strategy-2

The reaction needs many optimizations and has an excellent potential to establish chirality. In future, the first target is shape and size optimization as the homogeneity is very much essential to show the same type of chirality. The second step will be the reproduction of the reaction by using L-Cysteine and observe if the chirality is the exact inverse of the D-Cysteine or not. In the third step, the optimization of the concentration and volume of the amino acid is needed to establish a perfect protocol.

Though some researchers are focusing on the synthesis of the chiral nanoparticles, they are not much working on the green chemistry pathway to perform such chirality experiments. The process will be totally green, and the reduction rate will be slower than ascorbic acid.

Project- 02

‘One-step Synthesis of Differently Shaped Gold Plasmonic Nanoparticles’

Introduction

Though several pieces of research have been done on nanoparticle synthesis, still a lot of room is left for further studies. Nanoparticle chemistry is the most flexible inter-disciplinary topic that connects several topics of chemistry from organic synthesis[32] to radiochemistry.[33] It put the 'science' to the next level as it widens its area from hardcore catalysis to specific biomedicine sectors. In the field of catalysis, optics, nanomedicine, sensing, hybrid materials, solar cell,[34] battery,[35] etc., nanoparticles are massively used. The properties of the nanoparticles are entirely different from the bulk matter as the electron confinement on the different levels of the particles can tune several properties of the nanoparticles. The structure-properties relationship expends nanoparticle chemistry towards a new generation. Thousands of researchers across the world are working on the structures of nanoparticles to develop a large number of applications, from electronic semiconductors[36] to chemical sensors.

The nanoparticle synthesis is highly challenging because the proper chemistry behind the structure formations isn't properly established. Unlike organic or inorganic ligand synthesis, there is hardly pre-planned optimization or 'sketch' for the usual syntheses reactions. The proper chemistry behind the formation of nanoparticles is not revealed due to the lack of instrumentations. In the 1850's Michael Faraday[37] first synthesized gold nanoparticles from gold salt by phosphorus. From then to the present day, several theories, as well as conflicts, have been developed, but still, there is no such quantitative method for developing a perfect protocol. More specifically, the reduction rate of the gold salt determines the shape of the nanocrystals, but there is no calculative way to determine shape without performing reactions. Gold forms several plasmonic nanostructures like cube, bar, star, pyramid, octahedron, hexagonal plates, etc.[38] Different plasmonic structures have distant LSPR peaks and variable sensitivity to the SERS, biosensing. Besides shape, the size also has control on the plasmonic and other properties as the oscillating frequency always depends on the size of the particles.[39] Not only plasmonic, but small sharp nanoparticles also show much higher catalytic efficiency than larger blunt nanoparticles. In nano-bio interface, enzymes or bio-organic molecules prefers to attach to the high index facets of the nanoparticles. Though for catalysis, small nanoparticles are highly efficient, there are several reactions at the microscopic level where big

nanoparticles are needed to observe under the microscope. Some groups[40] performed organic reactions by capped gold nanorods in water solvent where the larger size of the nanorods was needed to observe the direction of the nanorods under the microscope. For photonics,[41] different colors of nanoparticles are used, and their chemistry is studied. So, a broad application demand is present for nanoparticles with varieties of shapes and sizes. Hence, after so many years of discovery, the synthesis field is so much pronounced. Also, most of the solution phase syntheses have occurred via the seed-mediated method, a costly two steps method. Besides searching for new shapes, another challenge lies in reproducing the old structure by following any of the one-step, less costly synthesis methods.

Although in an ideal case, according to Wulf's theory,[42] the shape of the single crystal of fcc metal should be like a polyhedron,[38] in reality, the shapes are far away from the polyhedron. In the solution phase synthesis, firstly, the equilibrium never reaches, and also the effect of twin defects and capping agents the deviation occurs from the Wulf's polyhedral. By using these deviations (twin defects, capping agents, temperatures) in different ways, a large number of homogeneous structures can be formed.

Skarbalak *et al*. classified nanoparticle synthesis into three basic steps, that are nucleation, generation of seeds, growth into nanocrystals consecutively. Though the complete mechanism of nucleation is still not clear, La Mar's[43] theory is well accepted where they claimed that in decomposition way, metal atoms are released and started to agglomerate into small clusters after reaching the supersaturation level. Then these small clusters come together to form nuclei. But for the reduced pathway, there must have two possibilities. Either the metal ions are reduced first to zero-valent atoms and agglomerate to form nuclei, or they are reduced to low valent ions, and the ions come together and then are reduced to form nuclei. The pathway depends on the reducing agents, capping ions, polymeric chains, etc.

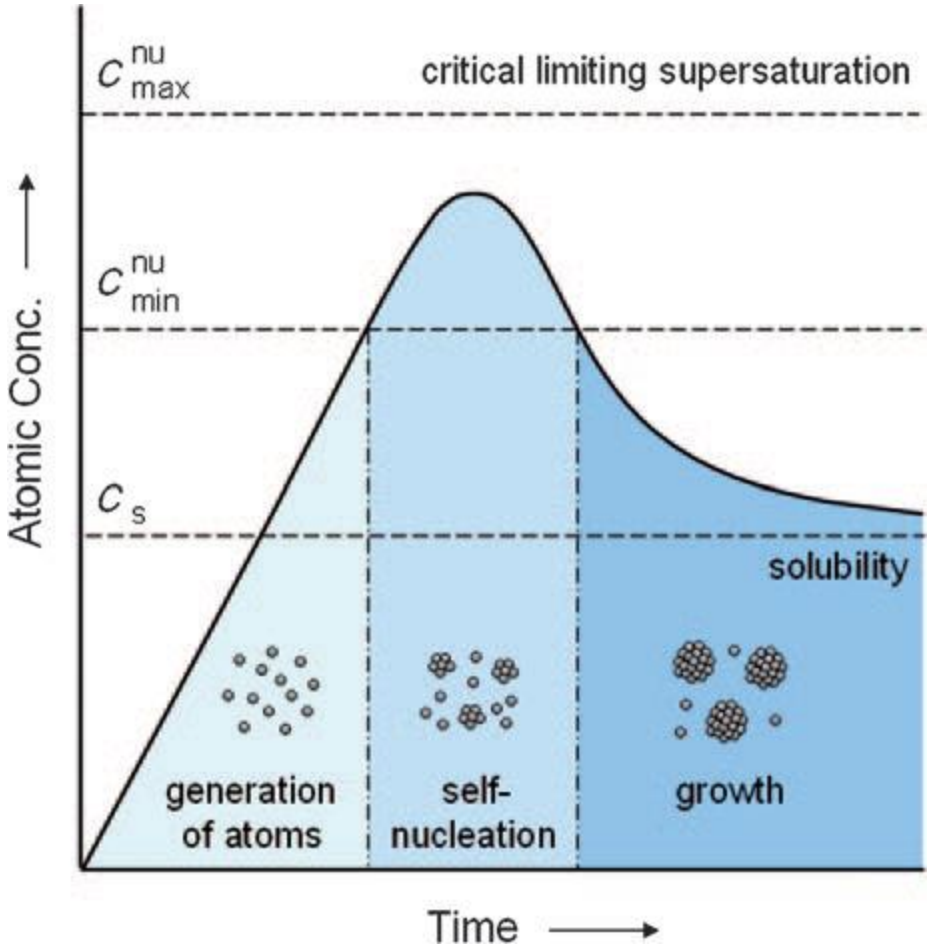


Fig 30. Schematic representation of the growth of the nuclei. (reproduced with permission from ref. [38])

After a certain growth of the cluster, the atoms are set properly, and the structures become locked and well defined, so no more atom can attach or detach from the cluster, that type of fixed clusters are called nano seed. Though the identification of clusters is highly challenging, seeds can be easily identified by the HRTEM. The pattern of the seed plays a great role in determining the structure of nanocrystals. Based on the arrangement, the seeds are usually classified into three major categories, which are single crystal, single twinned, multiple twinned seeds. Besides these three, the seed with stacking fault leads to form hexagonal or trigonal plate-like structures.

Different seeds lead to differently shaped nanoparticles. Single crystal seed leads to form octahedron, cuboctahedron, cube, bar, etc., whereas single twinned seed directs the reaction pathway to form bipyramid and beams. The twinned seed has a high strain on the structure, and the multiple twinned seed propagates the reaction to form decahedron and icosahedron.[44]

The synthesis mechanism either follows the thermodynamic pathway to minimize interfacial free energy or to follow the kinetic pathway to depend totally on the reaction rate. If we introspect the thermodynamic pathway, the most stable products should be formed. The different planes or facets have different energies, and thermodynamic product always makes the expansion of the high energy facets over the lower index facets. Hence the single crystal of fcc metal should form octahedral or tetrahedral structures rather than cube or others to maximize the [111] facets over [110] and [100]. But twinned defects can change the free energy conception as strain acts as an additional factor. For singly twinned seed, the free energy can be maximized when the structures are enclosed by [111] and [100] facets to form bipyramidal structures. But in the case of multiple twinned seeds, there's an angular strain of approx. 7 degrees, which makes the system destabilized. To minimize the strain and maximize free energy, icosahedral and decahedral shapes are preferable if the sizes are small as increasing the size causing to high strain and lower free energy.

The pathway turns kinetically controlled when the reduction rate of the precursor is significantly slow. The change in dynamic equilibria hampers the supersaturation level, resulting in the inclusion of stacking faults through hexagonal close packing. Due to such type of stacking fault, the seed converts into a plate-like structure much different from the polyhedral seed. The upper and the bottom surfaces are covered by the [111] facets leading to lower free energy and make the system highly energetic, which goes against the thermodynamic stability. By decreasing the rate of the reduction,[44] by using mild reagents,[45] using the Oswald ripening process,[46] the kinetic products can be intentionally achieved.

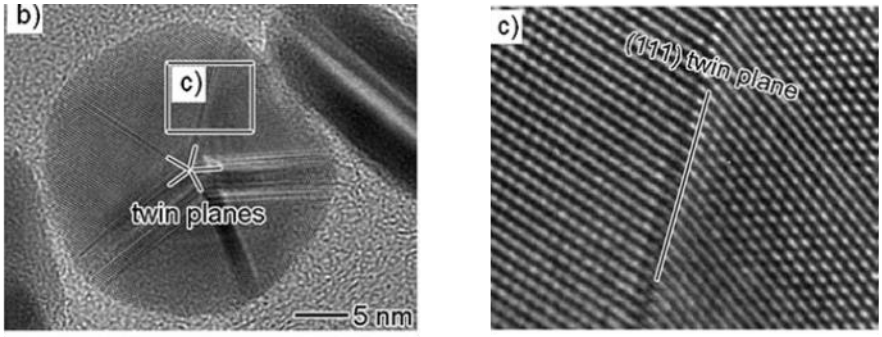


Fig 31. TEM images of Twin Plane b) Twin plane c) The common edges of Twin plane (reproduced with permission from ref. [38])

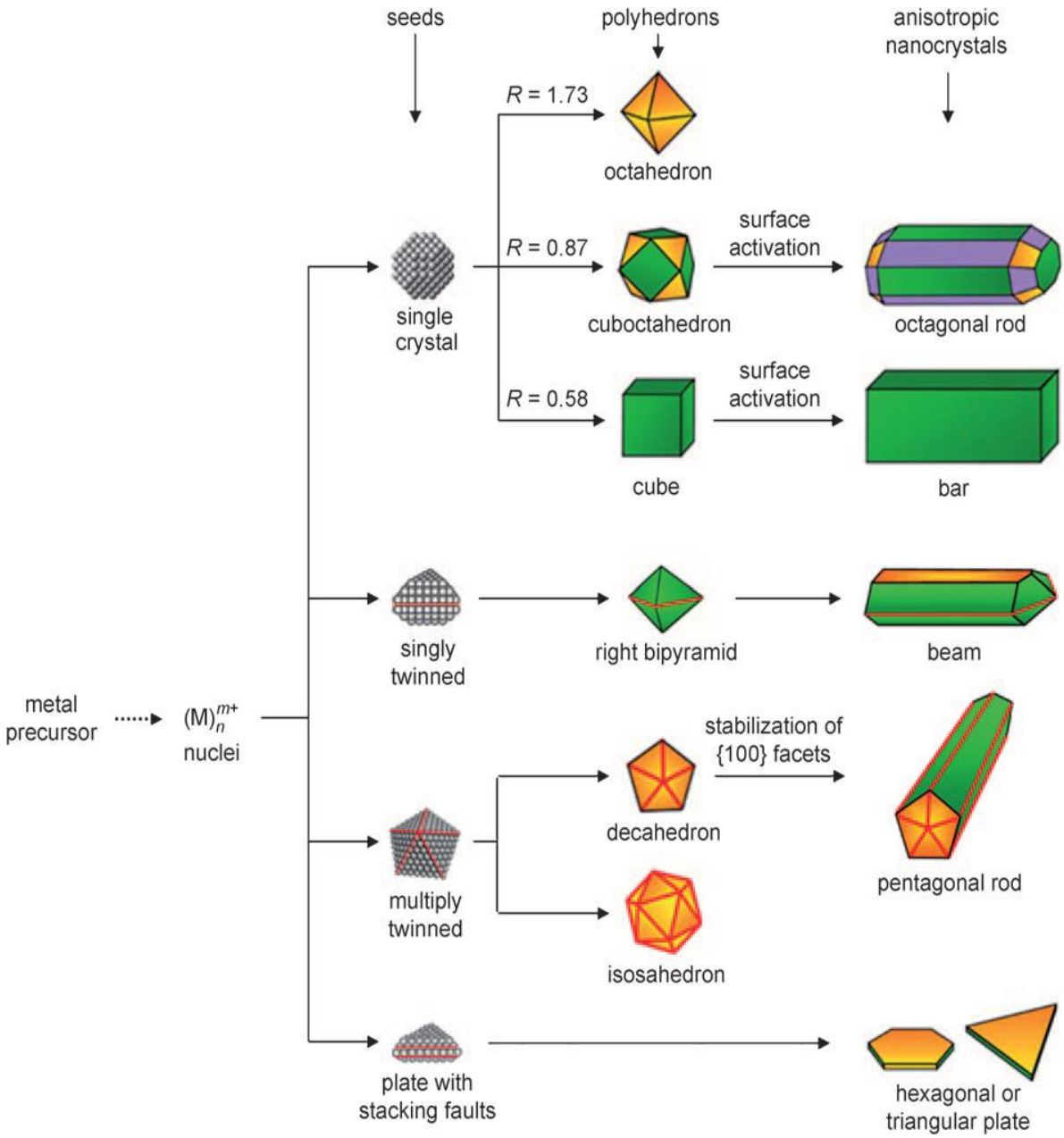


Fig 32. Schematic representation of the synthesis of nanocrystals from precursor (reproduced with permission from ref. [38])

The thermodynamics stability leads the structure formations toward octahedron and tetrahedron, but a large variety of shapes can be found by using the capping agent. Briefly, the role of the capping agent is to reduce or increase the free energy of a particular facet to shift the direction of the reaction towards a more energetically favorable pathway. In 1986, first Harris and team[47] reported that quasi-spherical particle turned into cubic shape when it was exposed to a very small amount of H_2S gas as we have discussed previously that the formation of [111] facets are much more favorable than [100] facets. But the interaction between gold [100] facets with sulfur makes the growth of [100] facets energetically more favorable, so the cube was formed. Different

capping agents are selective to the different facets to form different shapes. The commercially used capping agents are CTAB, CTAC, PVP, Citrate, etc. PVP attaches to the [100] facets and promotes ions to add on the other facets. The counter ions in the capping agents also have a great role in controlling the shapes. An experiment was held by Chad Mirkin *et al.*[48] where they have shown shifting from CTAB (cetyltrimethylammonium bromide) to CTAC (cetyltrimethylammonium bromide) the structure has completely changed from the elongated tetrahexahedron to the concave cube. The tetrahexahedron structures can be thought of as four pyramidal units on the four sides of the nanocube, and the concave cube structure can be imagined as someone cut the four pyramidal structures from the normal cubic shaped nanoparticle. This beautiful change can be monitored just by changing the counterion from bromide to chloride. There are some chemicals like CO, which can poison the one selective facet to stop the growth of these facets from creating a 'synthetic dead zone.'

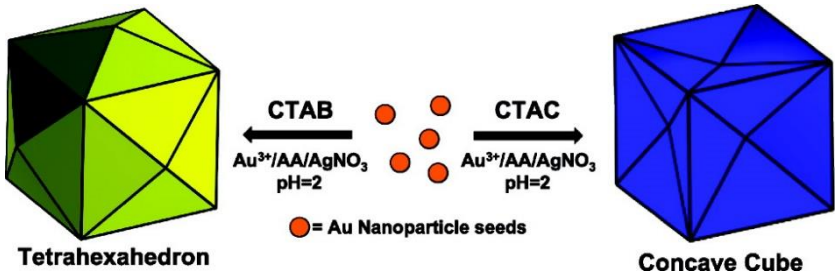


Fig 33. Schematic representation of the capping agent dependent shape changing (reproduced with permission from ref. [48])

In a typical seed synthesis, single crystal, as well as twin seeds, are also formed. The presence of the twin seeds can hamper the yield of our desired product and can shift the reaction dynamics to different reaction pathways. To control the type of seed, the concept of etching has come where in the presence of some ions and oxygen, twin seeds are converted into single crystal seeds. When the seeds are formed from the solution, the percentage of single-crystal seeds is also significantly higher than twinned seeds. Now due to higher strain, twin seeds are not so much stable, prone to redissolved or oxidized to the precursor solution[49]. Bromide and oxygen can oxidize multiple twin seeds, whereas chlorine can redissolve single as well multiple types of twin seeds. In the presence of chloride ions, all twin seeds can be removed in the polyol synthesis of Ag nanoparticles.

Besides the above-mentioned facts, sacrificial agents, temperature, solvent, impurities, and several other factors control the reaction pathway. There is no such ‘guideline’ for nanoparticle synthesis as nanoparticle synthesis is not only science; it is an art.

In the solution phase, it is challenging to synthesis high index facets, as to lower the surface energy, the high facets tend to disappear to form low index facets. As the low coordinated atom density is much higher on high index facets, these are very active for catalysis and molecular adsorption. Prof. OOK Park[50] and coworkers previously performed the studies where they have observed rhombic dodecahedron has transformed to octahedron via the formation of rhombicuboctahedron by controlling the concentration of PVP solution in water. They assumed that the high growth rate and the etching effect of the water make to hinder the high index facets. So, their target was to reduce the reduction rate as well as stop the etching. The beauty of the reaction is that they have only used PVP like cheap surfactant and DMF like very common organic solvent for reduction purposes. The concentration of the PVP was too high; it's about 1750 folds of the gold concentration and extended the reaction time to 8 hours. Briefly, they have added 8ml of 2.47 M of PVP-55000 solution and 0.12 ml of 94.6 mM of gold solution into the 3.88 ml of DMF. The vial was capped properly and set in the oil bath at 80^{o}C.

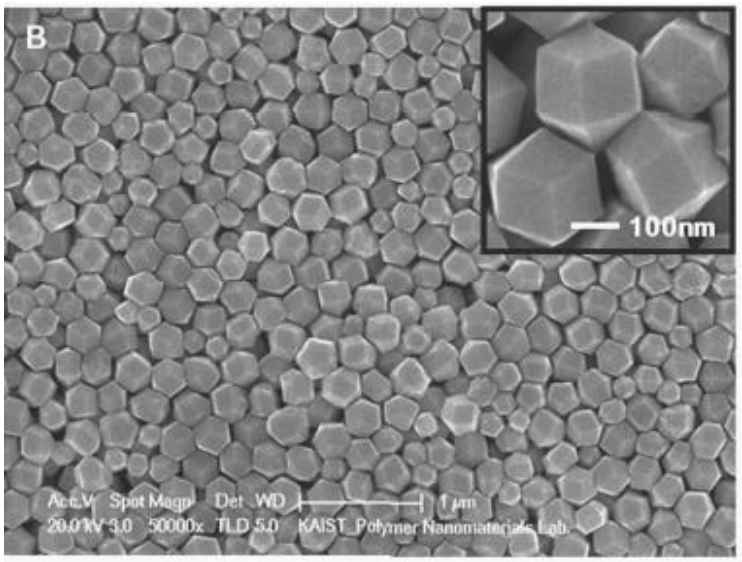


Fig 34. FESEM images of the THH (reproduced with permission from ref.[50])

At the initial stage, the color of the solution was light yellow, and gradually it changed to colorless solution to indicate the reduction of Au^{3+} ions reduced to Au^{+} ions, and at the

end hours of the reaction, the color of the solution turned orange to brown, the color of the nanocrystals. They have shown FESEM images of the nanocrystals at different stages where the facets are clear.

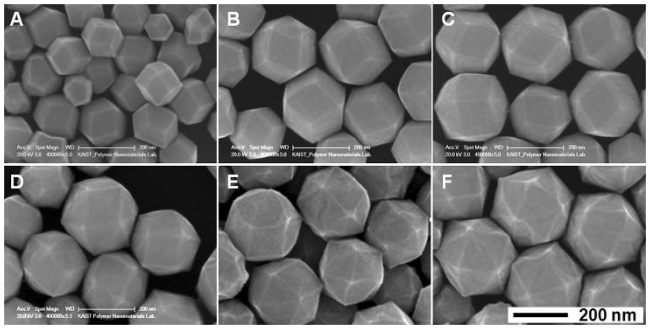


Fig 35. FESEM images of the different shapes of THH with time (reproduced with permission from ref.[50])

Motivations and Goals:

Synthesis of the differently shaped nanocrystals is still challenging and important to the science community as the shape and size can tune the plasmonic or optics properties, catalytic properties, sensing properties, SERS, etc.. The main motivations behind the work are discovering the newly shaped nanoparticles and reducing the cost and steps of the reaction. Sharp-edged or sharp corners containing nanocrystals are good for SERS sensing and catalysis, whereas for optics, optimized edged nanoparticles are more valuable. Hence for different purposes, different shaped nanoparticles are needed. For each shape, the plasmonic band gaps are different; hence there is a strong demand for various types of nanoparticles in the plasmonic field. For nanomedicine and ultra sensing, the refractive index sensitivity plays a significant role, and that refractive index sensitivity[51] depends on the shape and the structures. The dependence is not limited in the structure; size also has great control on these properties. So our motivation is also to control the size of the particles.

Prof. OOK Park *et.al* have synthesized gold tetrahexahedron nanoparticles of size 200nm approximately by using DMF as solvent as well as reducing agent in one-step synthesis method. Our goal is to change the reaction parameters to observe the changes in products. Firstly, the shape depends on the reduction rate of the gold salt, which is controlled by the ratio of gold salt and reducing agents. Secondly, the capping agents have high control on the facets, which eventually determines the shape. Thirdly, the temperature played an important role in his work and, lastly, the reaction time. These four parameters control the shape of the gold particles in OOK Park's work, and our goal is to change or alter these parameters to the synthesis of large, homogeneously shaped new nanoparticles. Inspired by the previous work on chiral nanoparticles, we planned to use amino acids in higher concentrations to change the shapes and sizes. Though we hardly found any shape-controlled work by amino acids in literature, we set up the experiments. In chiral work, Prof. Ki Tae mentioned that the higher concentration and volume of the amino acids lead to overgrowth and diminished chirality. We intended to find if amino acid has any control on shape and sizes. Also, the timing of the addition of the amino acids is important, and the results are different. When the amino acid was added at the beginning of the reaction,

the very small particles were formed, which were not even detected clearly through FESEM, but while we have added amino acids at the middle of the reaction that tuned the shapes. As the reaction is water-sensitive, so the concentration is also an important factor as the ‘Volume make up’ formula does not work in this reaction.

In the first approach, we have modified the gold concentration and the volume of the salt solution. In their work, they have used 94.6 mM of gold, whereas in our case, 100 mM of gold solution was used. After several optimizations and trial and error experiments at a certain limit of gold volume, the homogeneous structures were produced.

In the second approach, we have modified the reaction time at the optimized volume and concentration of gold solutions and got an optimized result. Again when the time modifications have been done by using original volume and concentrations derived by OOK Park, we didn’t get any different homogeneous nanoparticles. Also, the importance of time optimization is that it helps to understand the mechanism of the reaction.

In our third approach, we have varied the amino acids like cysteine, lysine, methionine. The concentrations and the volumes were studied and optimized. Different amino acids produced different results. The thiolated amino acids attach to the surface of the nanostructures or seeds. However, here we have observed that non-thiolated amino acids played a role in determining shapes and sizes, whereas thiolated amino acids do not show any significant result.

In the last approach, we have changed the type of PVP surfactant. All of the previous syntheses have been done by using PVP- 55000, whereas in the last approach, PVP-10000 has been used. PVP is a polymer, and the long-chain polymer has a higher molecular weight, whereas short-chain polymer has lower molecular mass. In both cases, we have taken the same weight of PVP and observed changes in structures.

My motto is to observe the changes in structures by modifying from the major changes to minor changes. The major changes are derived by changing the ratio of gold and DMF, changing time, and the minor changes are to changing the molecular weight of polymer surfactant, adding amino acids, etc.

Experimental Section:

Chemicals-

Poly- (vinylpyrrolidone) (PVP- MW: 55000), Chloroauric acid ($HAuCl_4$) were bought from Sigma Aldrich; poly- (vinylpyrrolidone) (PVP-MW: 10000), L-Lysine monohydrochloride, L-Methionine were purchased from SRL chemicals. Millipore water and 99.9% pure acetone.

Methods-

2193.33 milligrams of PVP were weighed in a 30 ml clean glass vial, and 11.8 ml of DMF was added. Two small magnetic beads were placed in the vial to create vigorous stirring, and the vial was kept on the magnetic stirrer to dissolve the PVP properly. If beads are stuck in the PVP, then sonication is needed to dissolve them. The oil bath was heated from 80^o to 85^o Celsius. The 125 µl of 100 mM gold solution were added, and the cap of the vial was closed tightly. After the required time, the hot vial was placed in ice to quench the reaction.

For different experiments, the ‘required times’ are different as for some reactions; we kept it for 7 hours, whereas some reactions need 16 hours to be completed. In the case of amino acid-mediated synthesis, 100 µl 10 mM amino acid solutions in water were added after 5 hours of the reaction.

The reaction is highly dependent on stirring, and the color of the solution changes to deep brown if the reaction goes perfectly. If the color of the solution changes to light reddish-brown or deep yellow, the reaction has not happened properly.

After quenching the reaction, the reaction mixture was taken in several mct of 1.5 ml and was centrifuged at 10000 rpm for 15 minutes. After decanting supernatant liquids, the mcts were filled with acetone and millipore water and sonicated to dissolve it. To wash the nanoparticles from PVP, these processes were performed a minimum 4 times.

Refractive Index Sensitivity Experiment-

R.I sensitivity experiment was performed by dissolving nanoparticles in glycerol-water mixtures of different ratio and observing the shift in absorption spectra. Five solutions were prepared where the percentage of glycerol in water were 0%, 20%, 40%, 60% and 80%. The same portion of the nanoparticles were dissolved in each solution and the shift in maxima was observed in UV-Vis spectroscopy. Then the known value of the refractive index of the mixtures were taken from an established data and plotted it in x axis and the maxima of the nanoparticles are put in y axis to get a best fit linear plot. The slope denotes the R.I sensitivity.

Results and Discussions:

Though our main motive was to observe structural changes by changing the reaction parameters, we channelized the parameters to produce a large number of homogeneous gold nanocrystals. From the increase of the size of tetrahexahedrons, we have broader our research horizon to syntheses completely different shaped nanoparticles like nano bar and others. We have developed the nanoparticles having concave as well as convex planes at a single site that may show high sensitivity towards biomolecules. Again we have studied the refractive index sensitivity to establish the nanoparticles as a good substance for the nano-bio applied field.

Size Tunning of Gold Nano Tetrahexahedron-

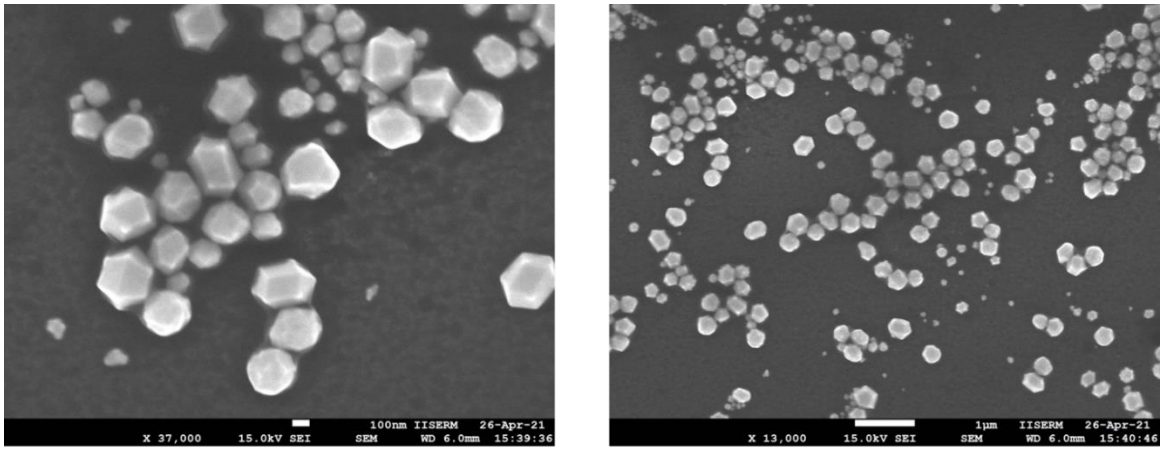
The tunning of sizes in one step synthesis process is challenging as there is no such seed-mediated way to control the size by varying the dilution of seed solution. The approach of increasing reaction time sometimes leads to overgrowth from the desired shape. Prof. Park and his team have synthesized the tetrahexahedrons of size nearly about 250 to 300 nm. After several modifications, we have established a protocol to increase the tetrahexahedrons' size from 500 to 600 nm.

We have used PVP (MW – 10 000) instead of PVP (MW- 55 000) as the surfactant, and added the 113 μl of 100 mM gold solution. After 5 hours of the reaction, the lysine solution was added, and the reaction was quenched after 9 hours.

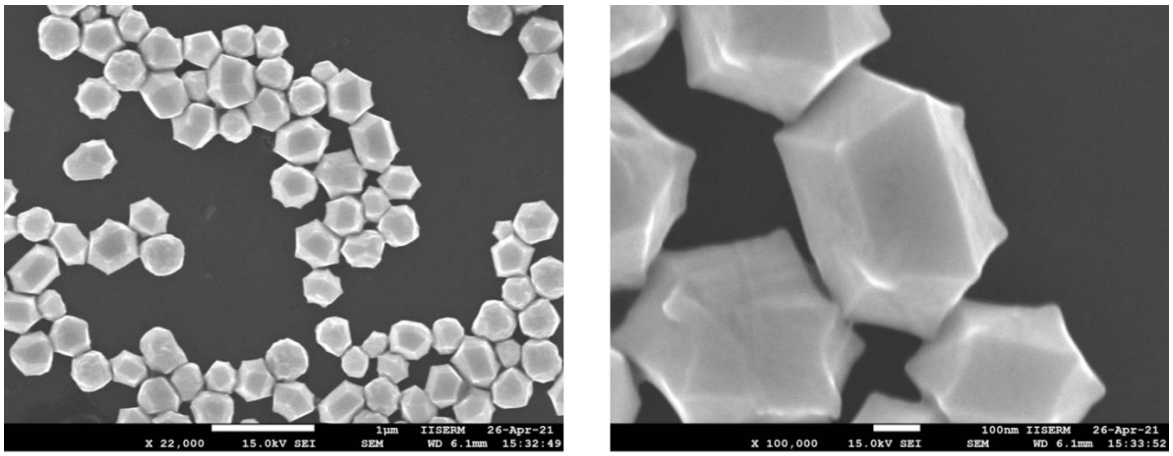
Some facet-developed spherical particles were present, and a very less amount of half-developed tetrahexahedron structures were also there. The established mechanism behind the formation of the structure indicates that small size cubic or cubic-like structures are eventually converted into polyhedral structures, which sometimes look like spherical with sharp facets. So it may be possible that these spherical-like particles were undeveloped nanoparticles.

The role of the lysine is still not clear here, and we are working on it. By changing the volume of the lysine from 100 microliters to 10 microliter, the yield of the THH structures has been going down. Not only the lousy yield but also there are several small structures, pentagonal structures were observed. Hence the volume of the lysine has a

significant role in the synthesis of this shape. We have performed another experiment where we have changed the gold concentration to 125 µl and did not add lysine or any amino acids. The structures were shifted to pentagonal and mixtures of cubic, spherical, and others.



10 microliter 10 mM Lysine was added



100 microliter 10 mM Lysine was added

Fig 36. FESEM images of tetrahexahedron

Synthesis of Gold Nano bars Having Slight Cleavage-

Though there are several established nano bar synthesis protocols, one-step synthesis is still challenging by using PVP like surfactant, which is 40 times cheaper than CTAC. The slight cleavage on the nano bar's side makes it special as there is a concave site is formed, which eventually changes the facet at the site. Our expectation is that small slight concave cleavage doesn't change the properties in a large way, but that site may increase the SERS

activities of the nano bar. The 'U' shaped cleavage may act as a pocket in catalysis by increasing the catalytic efficiency.

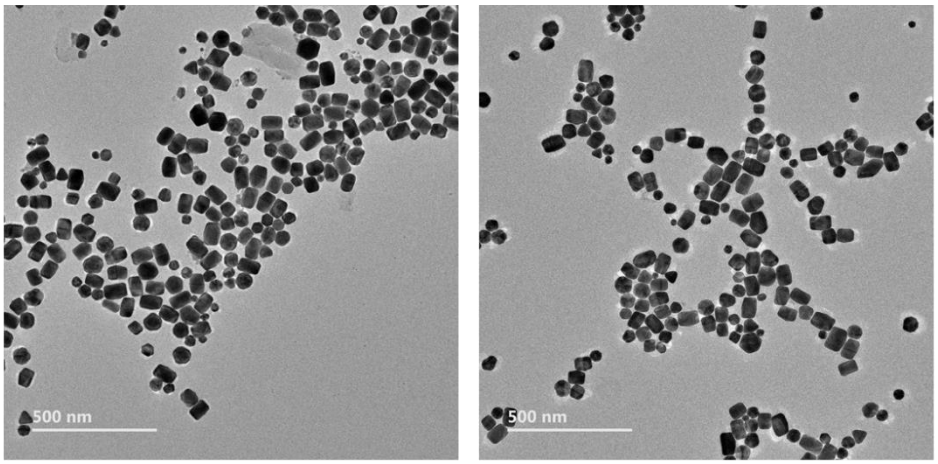


Fig 37. TEM images of gold nano bar with slight cleavages

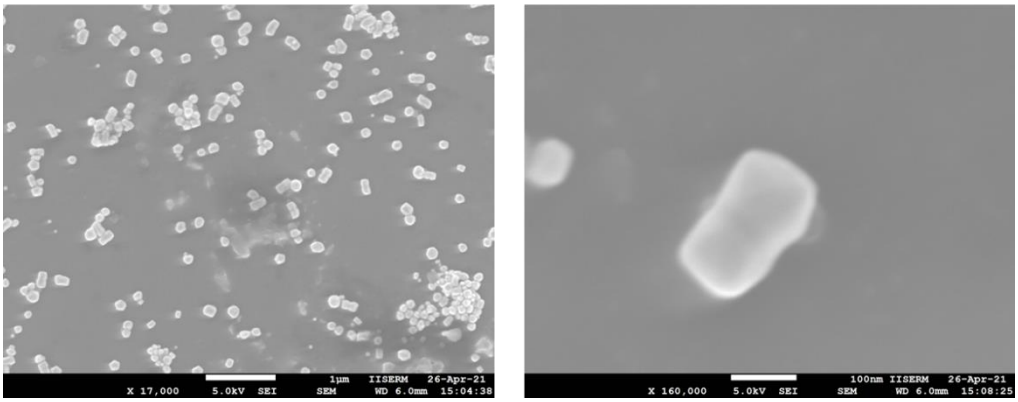


Fig 38. FESEM images of gold nano bar with slight cleavages

To synthesize these nanoparticles, PVP- 55000 was used as surfactant, and the 122 µl of gold solution was added to begin the reaction. After 5 hours, 100 µl Lysine solution was added, and the reaction was quenched after 7 hours.

The yield of the reaction is very high as approximately all of the particles were bar-shaped, and some of the particles were tilted due to the little deeper cleavage. In close introspection, some particles were observed as ‘D’ shaped due to higher tilt.

First, our thought was that Lysine galvanized the cleavage, but after doing controlled experiments and by using other amino acids, the present thought completely changed and reversed as Lysine protects the system from creating deep and multiple cleavages. In our next experiment, we will describe the deep cleavage structures where Lysine was not used. By replacing the Lysine with Cysteine, we obtained multiple and deep cleavage

structures. The role of the amino acid is still under investigation. In the future, we have planned to pursue volume optimization experiments from 50 microliters to 500 microliters of Lysine. But there's a major problem that the reaction is highly water-sensitive, so increasing the volume of the amino acids eventually increases the amount of water, leading to truncated tetrahedron as per established protocol.

Synthesis of Multi Cleavaged Structures-

Concave and Convex structures have massive utilities in various fields as the concave site creates very high facets compare to the normal structures. For example, concave cubes have many more high facets than the normal sharp-edged cube. Wang and coworkers showed the synthesis and plasmonic properties of convex cuboids. In our structure, concave and convex sites are present simultaneously.

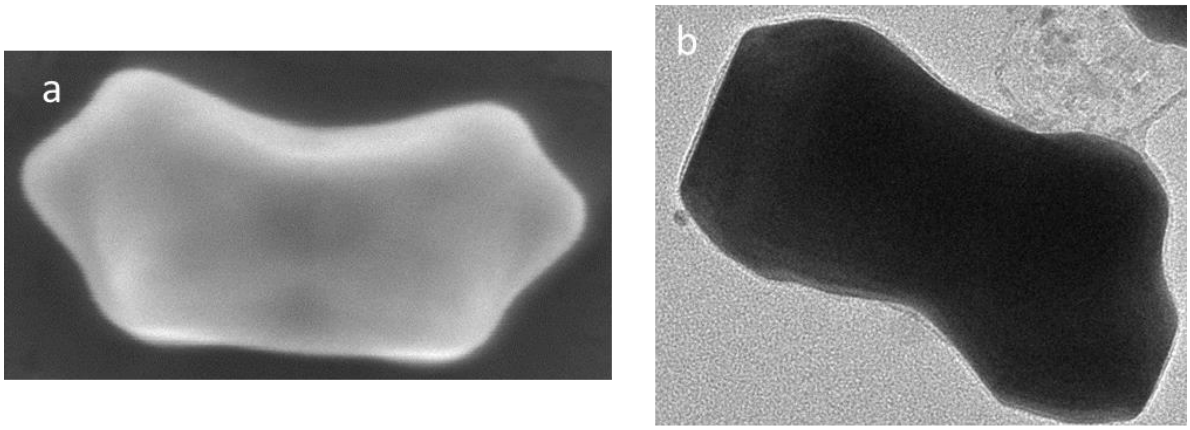


Fig 39. a) FESEM b)TEM images of multi cleavage containing nano bars

Wang *et al.* synthesized concave and convex cuboids, nano bar from gold nanorods using Cu^{2+} and varying the surfactants mixture ratio. But in our case, the synthesis is one step, and we have used PVP instead of costly surfactants like CTAC, CTAB, BDAC. In these structures, the convex sites and concave sites are present periodically. Although three to five numbers of each concave or convex site are varied in a single nanostructure, most of the structures contain four concave or convex sites. The number of concave and convex sites is equal because linear planes are also present in the structures.

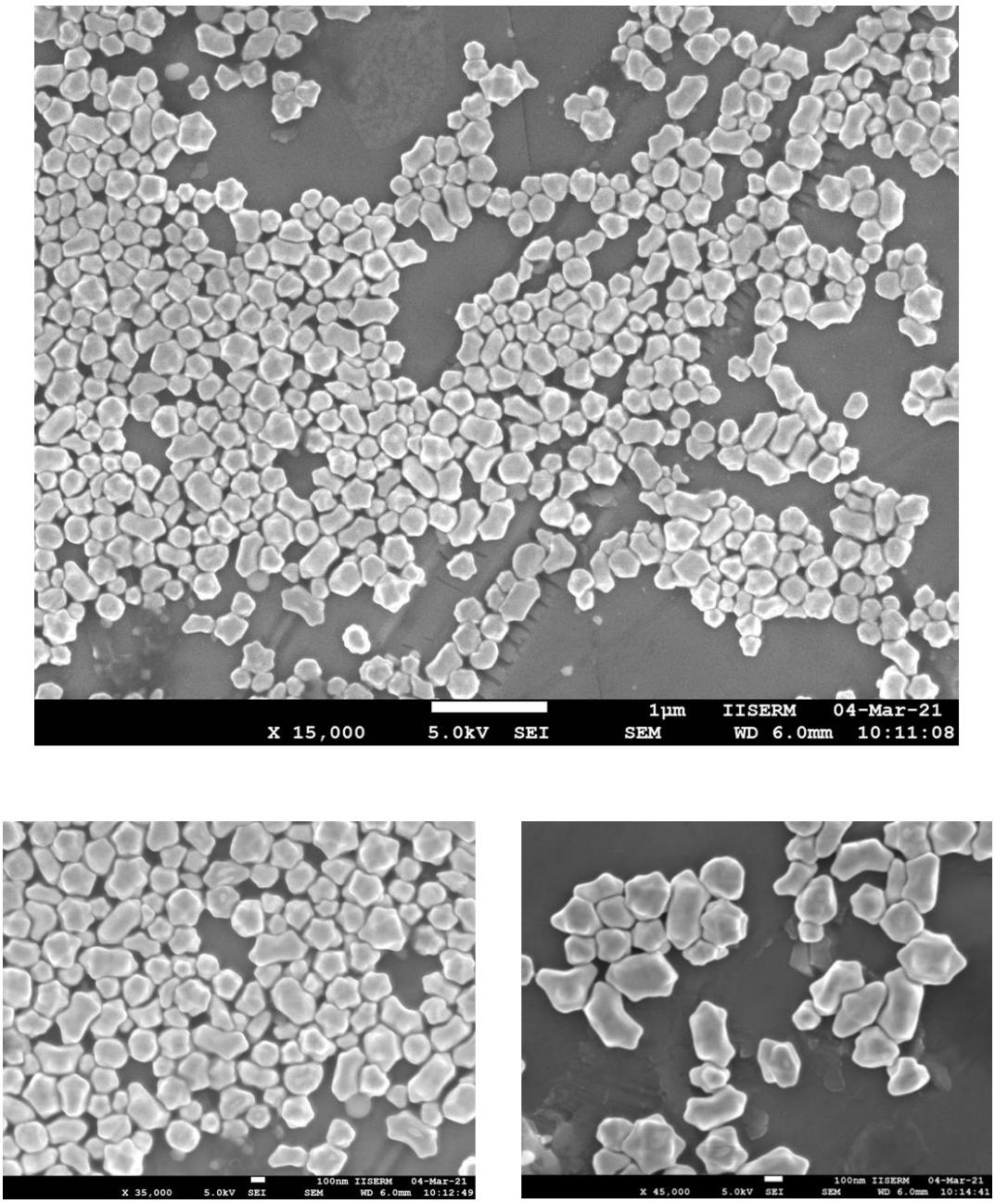


Fig 40. FESEM images of the multi-cleaved nano bars

To synthesize these structures, 106 µl of the gold solution were taken in the PVP 55000 solution, and the reaction was quenched after 16 hours. No amino acid was added to the reaction, and the reaction was prolonged to 16 hours to get a large number of multi cleaved nanostructures.

Previously, when the reaction has occurred for 10 to 12 hours, there were some nanoparticles with sharp-edged (boat-shaped) implies the very less concave or convex sites. Our understanding was with increasing the reaction time; the cleavages would be deeper as we got a very less number of propellor-shaped nanoparticles. In the motive to increase the cleavage to synthesize propellor-shaped particles, we have increased the reaction time. But as a result, there was no evidence of deeper cleavage, but the convexity generates with the formation of more cleavages in the particles.

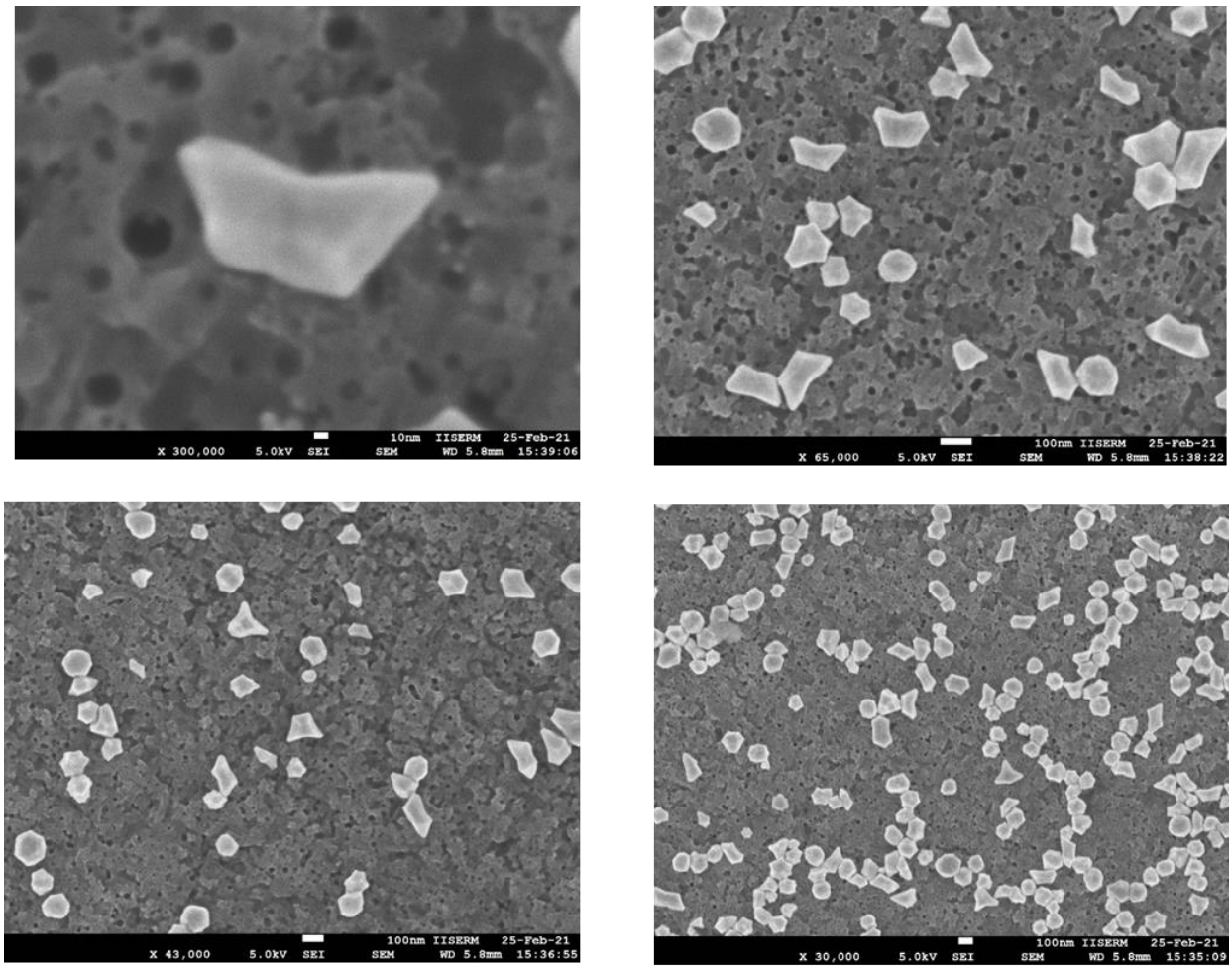


Fig 41. FESEM images of the multi-cleaved sharp-edged nano bars (boat-shaped)

These structures have also importance due to sharp edges though these haven't significant concave planes. Here is the switching from boat forms to concave and convex forms by increasing the reaction time.

These reactions were first performed with cysteine solution and the result was same. At that point, we have started to investigate the reason behind cleavage. Then after doing same reaction without the aqueous solution of cysteine or any solution the products were exactly same.

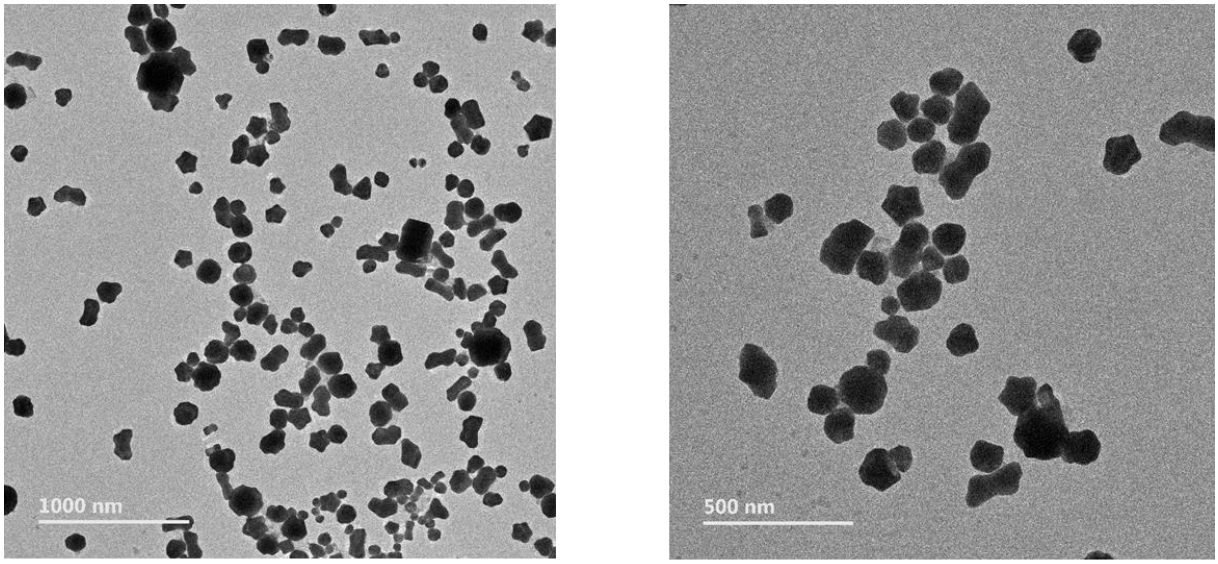


Fig 42. TEM images of cleaved nano bar after addition of Cysteine

Refractive Index Sensitivity –

In the motive to understand the bio sensing ability and to use in nanomedicine like highly important field, the refractive index sensitivity experiments were performed. The approximate R.I sensitivity value is 394.

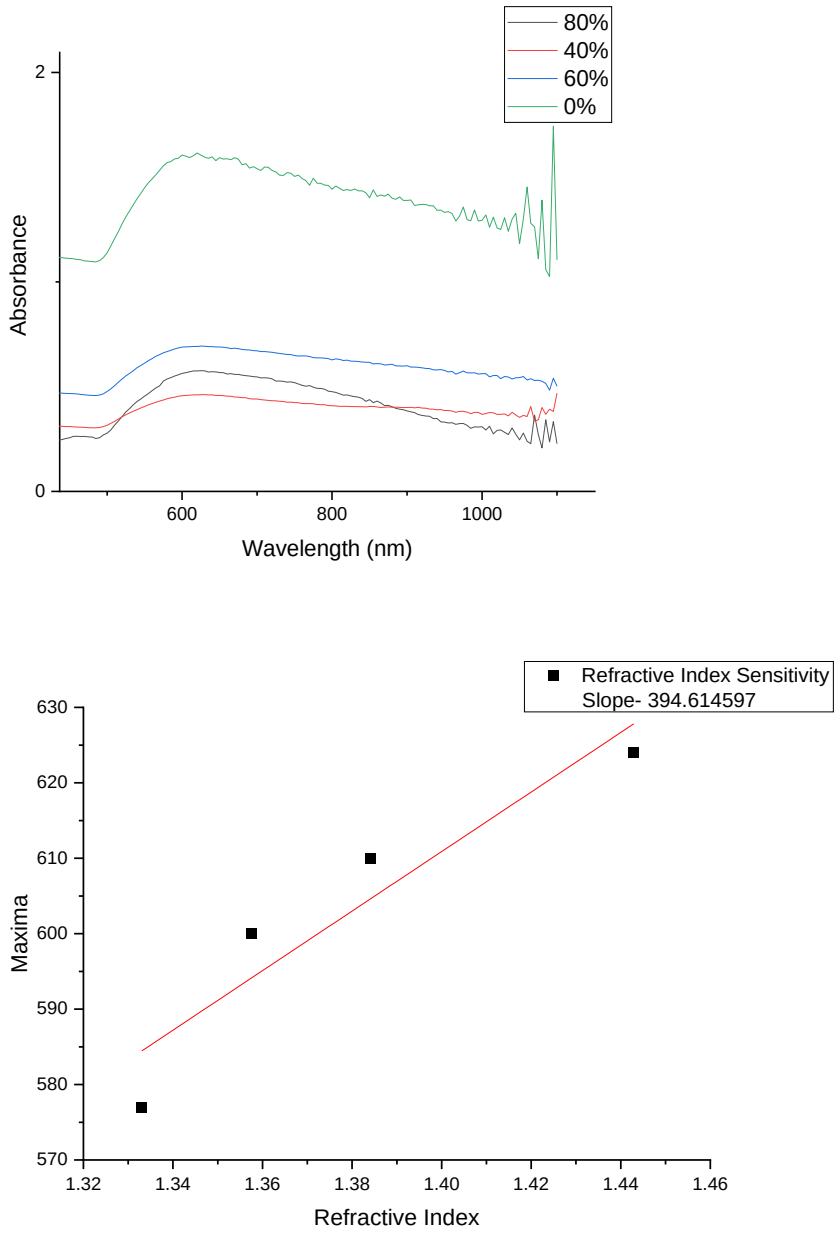


Fig 43. Refractive index sensitivity plot of maxima and Refractive index

Synthesis of the Octahedral Structures-

The idea behind the choice of amino acids in the presence of partially negative polarized center or lone pairs as Cysteine, Lysine both have lone pairs on the sulfur center or nitrogen center. The lewis acidic property of gold is well established and has been tremendously used in organic catalysis. Reducing agents were reduced Au^{3+} ions to Au^{+} ions to Au atoms so if there is any negatively polarized center that may interact with golds. Unlike lysine and cysteine, methionine does not have any 'SH' group, but the investigation was performed to observe as it has an 'S-CH3' group. Though the mechanism is still under investigation, pyramidal and cubic structures were produced by using methionine.

146 µl of the gold solution was added into the PVP (MW- 55000) solution, and methionine was added after 5 hours. The reaction was quenched after 8 hours to produce the mixture of octahedral and cubic shapes.

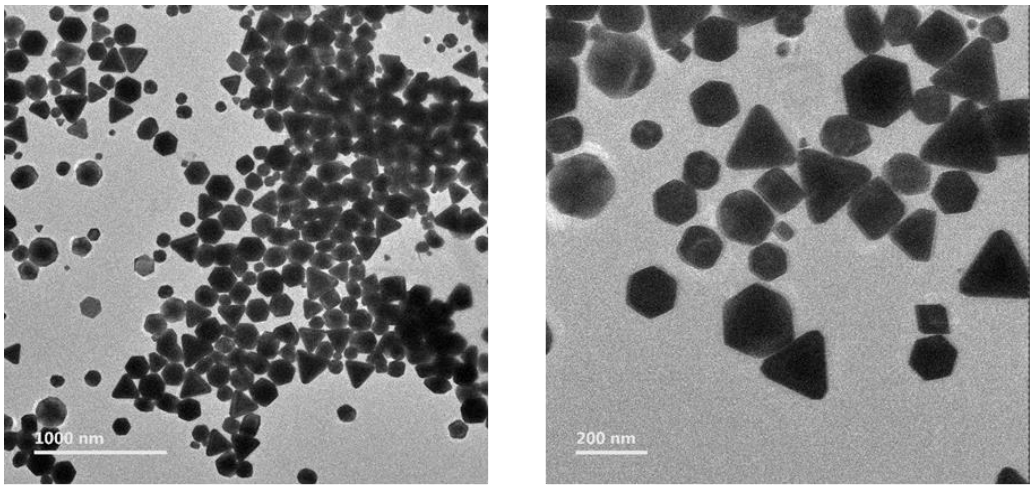


Fig 44. TEM images of the methionine mediated synthesized nanoparticles

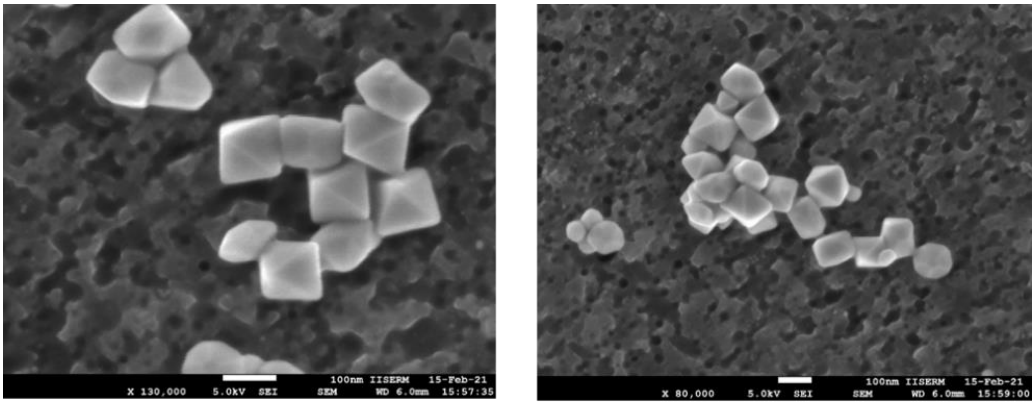


Fig 45. FESEM images of the methionine mediated synthesized nanoparticles

Synthesis of Gold Pentagonal Nano Structures-

From the curiosity to observe the role of PVP (MW- 10000) in the same reaction instead of PVP (MW- 50000), we have performed this test. 120 µl of the gold solution were added to the reaction, and the reaction was quenched after 12 hours to observe different types of structures.

Many pentagonal structures were produced, and surprisingly, there was no sign of that cleaved structure! There were other spherical, and some cuboid structures were observed, with the pentagonal species having 100 nm length. The yield of the pentagons was not so high, but in the future, we will try to optimize the reactions to get a high yield. Also, the study, carries the importance of slightly changing the condition to observe a significant change.

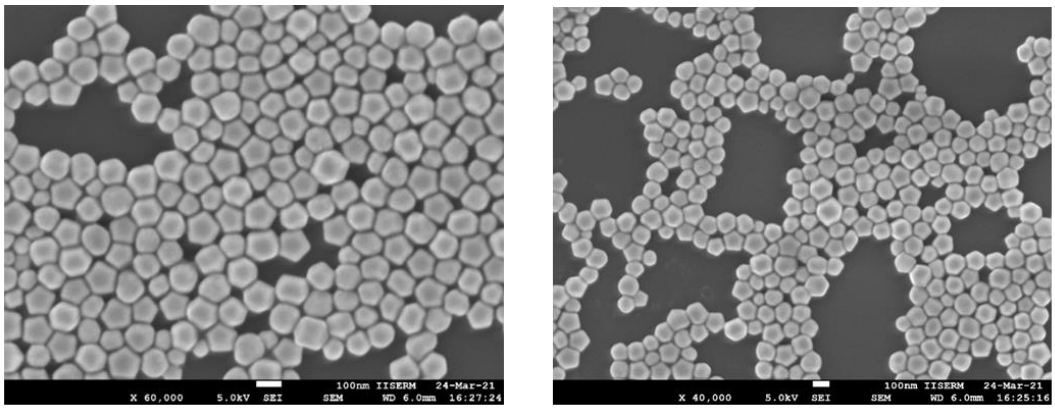


Fig 46. FESEM images of pentagonal structures

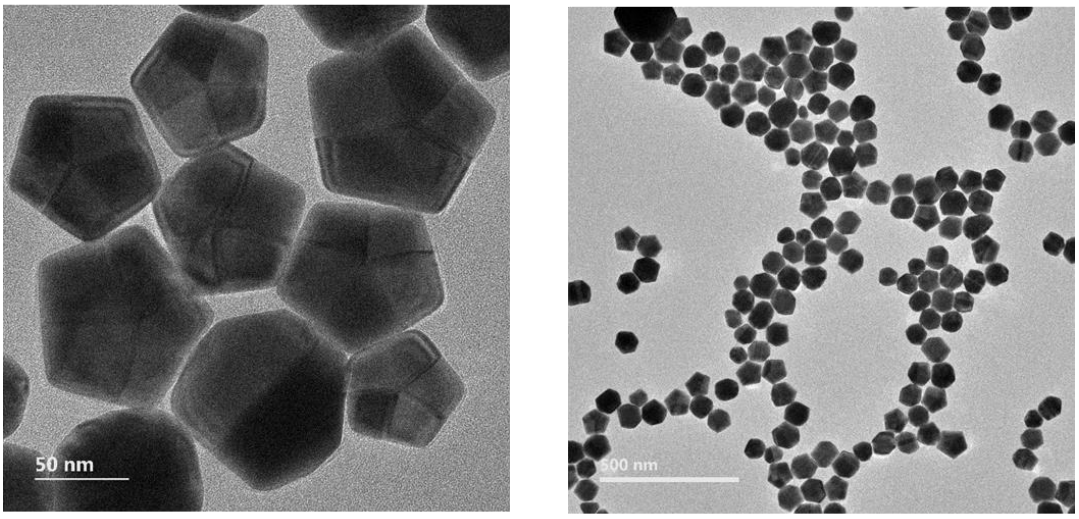


Fig 47. TEM images of pentagonal structures

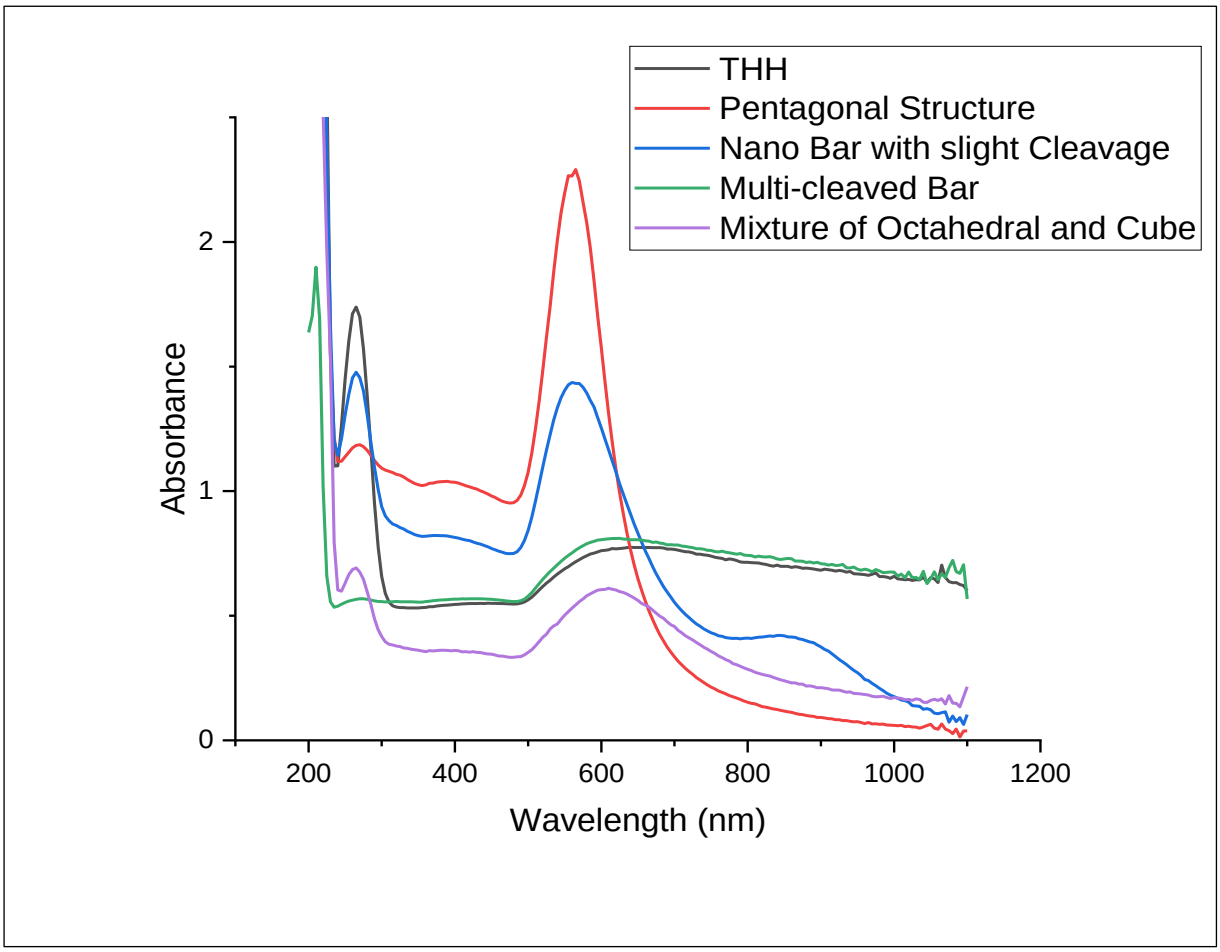


Fig 48. The UV-Visible absorption spectra of synthesized nanocrystals

The UV-Visible spectra indicates the possible plasmon peaks in the nanocrystals. Usually the bar like or anisotropic nanocrystals show two plasmon peaks, one for longitudinal and other for transverse.

Conclusions:

In this project, we have successfully synthesized five different shapes of gold nanoparticles just by modifying the reaction parameters. By using PVP-10000 and lysine solution, the tetrahexahedrons were synthesized which length is near about 500 to 600 nm. Whereas without the presence of lysine, varying the gold salt volume we got twin pentagonal structures of 50 nm. Again modifying the gold salt concentration and increasing the reaction time, a lot of multiple cleaved nps are formed which have concave as well as convex sites simultaneously. Shifting from PVP-10000 to PVP-55000 and varying the gold volumes and reaction times, nano bar with slight cleavages were formed after the addition of lysine, whereas methionine leads to mixture of cubes and octahedrons. The reaction is highly water sensitive and the vigorous stirring is highly required.

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