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8. Self-Assembly

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8.1 Introduction:

Self-assembly is a ubiquitous phenomenon in biological as well as non-biological systems. By this process, the smaller individuals seemingly organise into ordered structure, without the intervention of any external sources.[1] This can be understood from its two components. The first component *i.e.* self indicates that "spontaneous process" and the second component *i.e.* assembly indicates that "association, aggregation or forming together". Therefore, self-assembly of nanostructure is an assembly process that atoms, molecules or building block of nanoscale materials spontaneously organize into highly ordered structure or pattern in the nanoscale region without intervention from external sources. Nanoscale structure self-assembly occurs due to presence of supramolecular interactions between the individual components such as van der Waals, ionic, hydrophobic, hydrogen bond and coordination bond. The presence of these fundamental interactions in the individual components makes it highly ordered structure upon establishing the equilibration between assembly or non-assembly state of the individual component. These structures are currently well understood and can be controlled in order to get the desired functional properties of the self-assembly nanostructures.[2-3] The synthetic strategy is pretty much similar to the synthetic strategy of micro/macro and nanoscale materials.[4] The major aim of this book chapter is to illustrate the self-assembly of gold nanoparticles with different organic moiety assisted and its next-generation applications in biomedical as well as in electronics.

8.2 Small Organic Molecule Assisted Self-Assembly of Gold Nanoparticles:

Fullerene is a carbon cluster molecule and hydrophobic in nature. It has to be functionalize in order to make it hydrophilic in nature by introducing heteroatom like oxygen and nitrogen. One way to functionalize with well-known Prato reaction and synthesize N-methylfulleropyrrolidine derivative. This N-methylfulleropyrrolidine derivative was mixed with synthesized citrate capped gold nanoparticles with a certain ratio and assembly was increases with increasing the ratio *i.e.* the ratio of concentration of N-methylfulleropyrrolidine derivative to the concentration of citrate capped gold nanoparticles. This assembly was occurred due to interparticle charge transfer-induced and governed by van der Waals interaction. The fullerene-C_{60} surface contains 8 ring of pyrrolidine moiety and can extend the ordered structure in all possible direction upon equilibration established (*cf.* **Figure 1**). This assembly was pH tuneable and observed at 5.0-6.8 only.[5] It was also investigated with 3-mercaptopropanoic acid for assembly process of this fullerence-C_{60} derivative and was observed the similar phenomena.[6] Nucleophilic addition reaction strategy can be used for functionalization of fullerene-C_{60} with 1-methylpiperazine and synthesized 1-(4-methyl)-piperazinyl fullerene (MPF). This would be hydrophilic in nature and neutral molecule. This functionalized fullerene derivative can generate positive charge on the nitrogen of 1-methylpiperazine moiety with tuning the pH of the solution medium. The citrate capped gold nanoparticle possess negative charge on its surface ligand. This mixing of these two in certain ratio can harvest highly ordered 3-dimensional architecture. This assembly process was pH tuneable.[7-8]

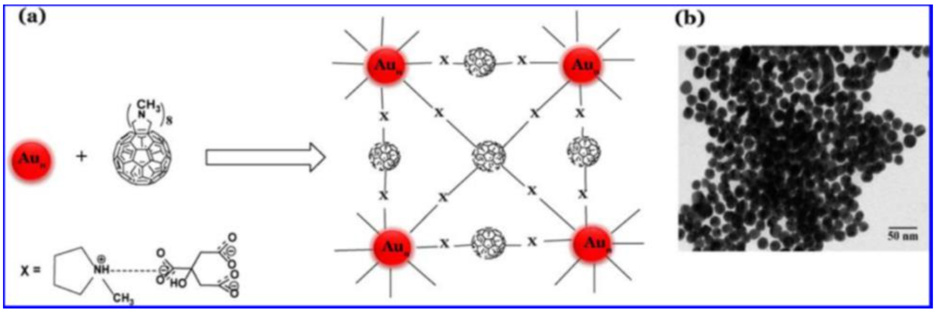

Figure 8.1: The interparticle interaction between N-methylfulleropyrrolidine derivative with citrate capped gold nanoparticles (a). The TEM micrograph of the corresponding assembly structure (b). Reprinted with permission from Ref. 5. Copyright 2007 American Chemical Society.

An interparticle linking agent tetradentate thioether, the *tetra*-[(methylthio) methyl] silane $Si(CH_2SCH_3)_4$ (TTE) was found to be assist for novel spherical assembly of gold nanoparticles. Tetraoctylammonium bromide capped gold nanoparticles were assembled due to interaction of tetradentate thioether and ligand place exchange reaction with dodcanethiol did not harvest the assembly structure, instead dis-assembly would be occurred. It did not observe any assembly of dodecanethiol capped gold nanoparticle with the tetradentate thioether. This indicated the assembly is ligand directed process and suitable chemical moiety should be present in the chemical structure of the ligand.[9] Homocysteine is an amino acid containing thiol, amine, and carboxylic group in the chemical structure. The thiol will oxidize to increase the stability of nucleation process of gold nanoparticle and surface layer would be present amine and carboxylic acid group for tailoring the assembly process. It was established that the driving process for assembly was due to interaction of negative charge on oxygen of one homocysteine capped gold nanoparticle with the positive charge of nitrogen of another homocysteine capped gold nanoparticle (*cf.* **Figure 2**).[10] In all the small organic molecule assisted gold nanoparticle assembly is characterized by decrease the absorbance of surface plasmon resonance at 520 nm and gradual evolution of increased absorbance at greater wavelength than surface plasmon resonance. Additionally, the physical appearance *i.e.* colour of the suitable ligand capped gold nanoparticle was also changes with assembly process. It was also estimated that interparticle distance by density functional theory (DFT) calculation and found to be 3.23 Å.[5]

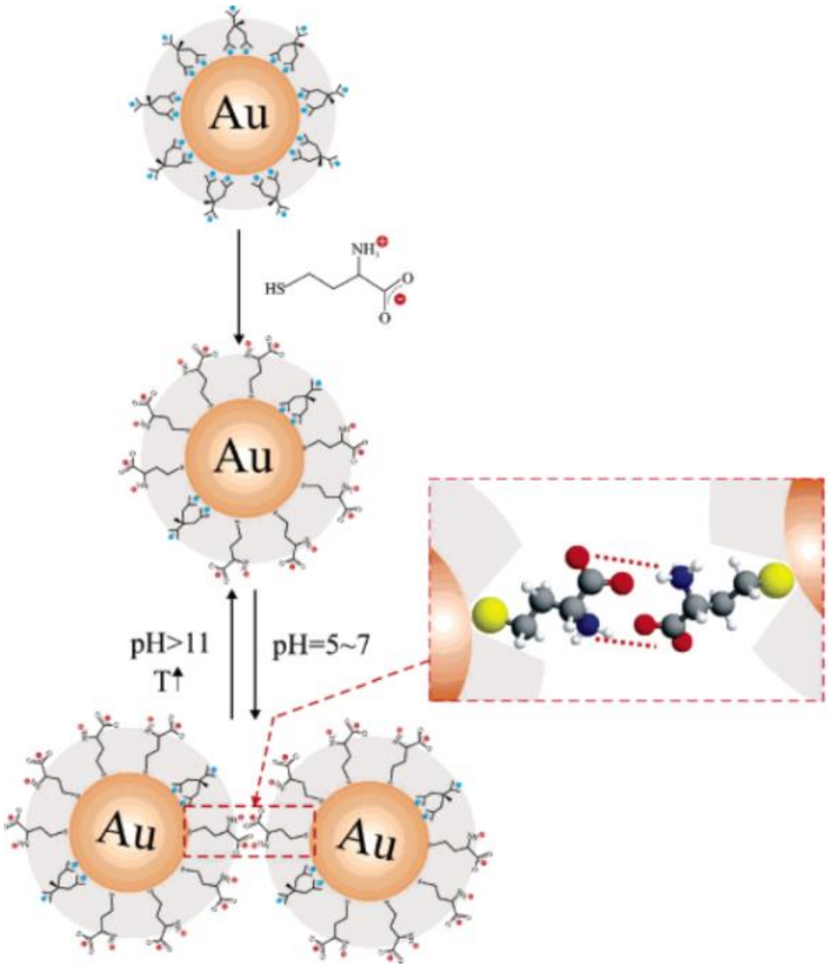

Figure 8.2: The interfacial interaction between the homocysteine capped gold nanoparticles. Reprinted with permission from Ref. 10. Copyright 2007 American Chemical Society.

8.3 Polymer Assisted Self-Assembly of Gold Nanoparticles:

Polymers are multiples of simple chemical monomers. The various functional moiety on to the polymer can be introduced in order to functionalize. The functionalized polymer can be polarized or generate charge by chemical modification or tuning the pH of the medium and can act as a source of binding site of ligand capped gold nanoparticles. The linear and periodic polymer has alternating ionic and polar sequences in the dilute concentration of polymer. The periodic polymer consist of alternated cationic poly-L-lysine (PLL) blocks and polar sequences of poly (ethylene glycol) (PEG) of varying chain length was used as a linking agent to assemble the 11-mercaptoundecanoic acid capped gold nanoparticles (*cf.* **Figure 3**). It was taken the advantage of positive charge on polymer side chain and negative charge on the monolayer of 11-mercaptoundecanoic acid capped gold nanoparticles.[11] The azo-benzene has ability for cis-trans isomerization due to □-□* transition and can be tuneable with the application of ultraviolet (UV) light. The trans-isomer can't induce assembly process due to presence of phenyl ring on either side and on the other hand *cis*-isomer induces assembly process due to increased shell polarity and thereby switches the solubility. The azo-benzene moiety can be introduced chemically into the polymer structure along with reversible addition–fragmentation chain transfer-(RAFT-) polymerization using 2-cyano-2-propylbenzodithioate as a control agent. The citrate capped gold nanoparticle would undergo ligand place exchange reaction with azo-moiety containing polymer and under UV light (365 nm) the polymer shell on to the gold nanoparticle changed structure from trans to cis. This cis transformation assisted in the formation of assembled structure and could be easily identified by the UV-visible spectroscopy. The assembled structure sedimentation would occur and could easily be identify by comparing the *trans*-isomer absorbance and *cis*-isomer absorbance.[12] The wrinkles as an external template can be used as linking agent for the assembly process due to their excellent scalability and high precision. The gold nanoparticle can also be used for assembly process but it is less colloidal stable due to aggregation during the drying process. This instability can be overcome by functionalizing the gold nanoparticle surface such as poly(N-isopropylacrylamide) (PNIPAM), poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT/PSS), poly(vinyl pyrrolidone) (PVP), poly(ethyleneglycol) (PEG) layers, and bovine serum albumin (BSA) protein layer.[13] The dodecanethiol-stabilized gold nanoparticles were assembled during the polymerization reaction between diglycidylether of bisphenol A (DGEBA) and dodecylamine (DA) due to presence of dodecyl chains in both components. This allowed to stabilize due to strong hydrophobic-hydrophobic interaction. The desorption of dodecanthiol from gold nanoparticles has taken place followed by coalescence of nude gold nanoparticles to produce larger sized gold nanoparticles with narrow size distribution of the nanoparticle. This phenomenon could be attributed from the broadening of the absorption spectra to the red shift. The diglycidylether of bisphenol A (DGEBA) and dodecylamine (DA) precursor can be used for self-assembly of other suitable nanoparticle containing long alkyl chain for interaction stability.[14]

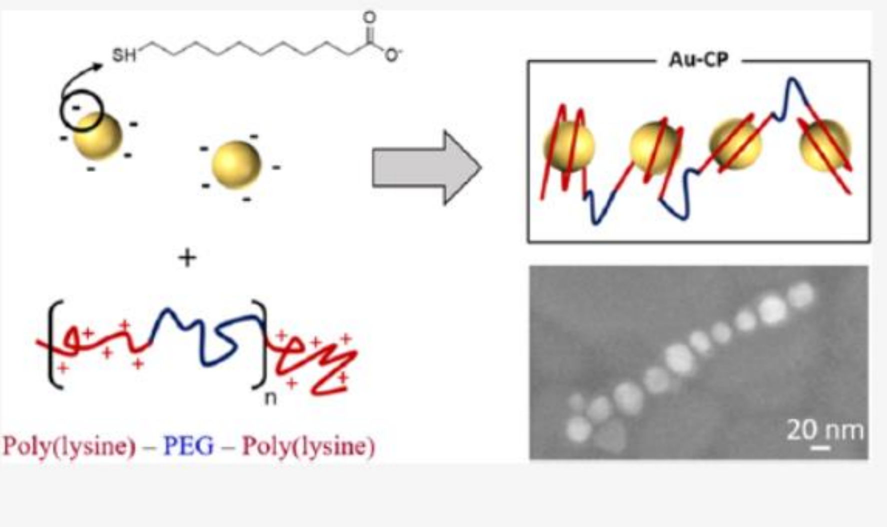

Figure 8.3: Assembly strategy between functionalized periodic polymer and 11-mercaptoundecanoic acid capped gold nanoparticles. Reprinted with permission from Ref. 10. Copyright 2020 American Chemical Society.

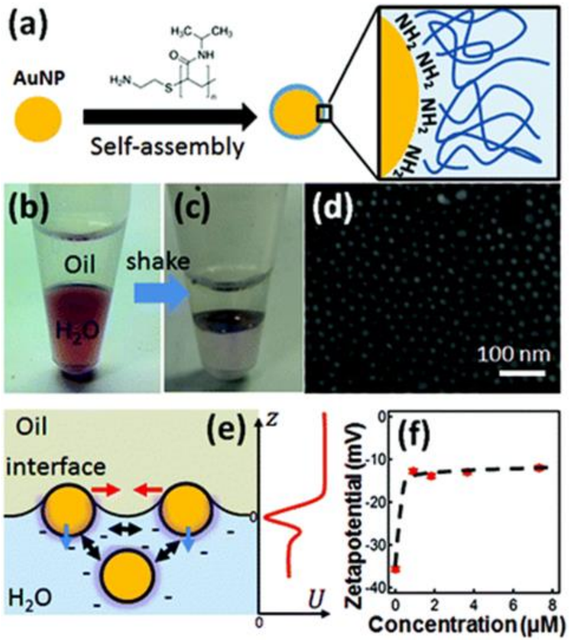

Figure 8.4: Strategy for polymer assisted gold nanoparticle assembly (a) and their colour changing from non-assembly state (b) to assembly state (b) with their corresponding SEM image. The interaction forces near the liquid-liquid interfaces *i.e.* capillary and van der Waals attraction (red), electrostatic and steric repulsion (black), solvation and line tension (blue), red curve (right) (d). The zeta-potential with the variation of concentration of gold nanoparticle assembly (f).[15]

The temperature induced assembly of gold nanoparticle was achieved by using amine terminated Poly-N-isopropylacrylamide polymer. It was well established that this polymer has temperature responsive characteristics. It was taken this characteristics advantage for self-assembly of citrate capped gold nanoparticle and could accelerated the process by cooling and heating for several cycles in order to get the thermodynamic equilibration with the aqueous phase. The addition of hexadecane solvent helped in precipitate out the gold nanoparticle at the liquid-liquid interface through vigorous shaking. The decrease of surface charge by using poly-N-isopropylacrylamide could replace the citrate ligand from the gold nanoparticle was evident from the zeta-potential study (*cf.* **Figure 4**).[15]

8.4 Surfactant Assisted Self-Assembly of Gold Nanoparticles:

A variety of surfactants have been used for the controlled synthesis of gold nanostructures owing to the presence of different head groups, hydrophobic chains, counter ions, and unique molecular structures. The critical micelle concentration (CMC) plays a critical role for the controlled synthesis of gold nanostructures which can be defined as the minimum concentration above which the micelles start to form. The siloxane surfactants are amphiphilic in nature with methylated siloxane hydrophobe coupled with one or more polyoxyethylene (EO) polar groups. This amphiphilic nature assisted in stabilising gold nanoparticles and also induced the gold nanoparticle assembly due to presence of one or more polyoxyethylene (EO) polar groups. It was believed that mechanism of formation self-assembly proceeded in two steps *i.e.* first step is the formation of amphiphilic surfactant stabilized gold nanoparticle and second step is the self-assemble to form linear aggregate due to non-uniform distribution of stabilizers on the nanoparticle surface. It was also observed that the ionic strength of the medium affects the assembly of the charged gold nanoparticles and increased assembly occurs due to increasing the concentration inorganic salt.[16] The separation of metallic nanorods are very challenging due to incomplete separation or purification. This can be overcome by using surfactant which allow a relatively simple and efficient method for separation of nanorods from a mixture of rods, spheres, and platelets. Gold nanorods were separated out when cetyltrimethylammonium bromide (CTAB) surfactant was added to the concentrated dispersion of a mixture of different size rods, spheres and platelets. It was found that the larger sized nanorods were precipitated out first and then smaller sized nanorods followed by platelets. These structures are thermodynamically stable because of gaining in translational entropy compared to the orientational entropy related with nanoparticle arrangment.[17] The citrate capped gold nanoparticles were assembled to form nanochains and formation of this nanochains was encouraged by the addition of CTAB surfactant. The different concentration of the surfactant leads to different architecture due to different interparticle interaction (*cf.* **Figure 5**). The suitable concentration of CTAB acts as glue that could link the (100) facets of two neighbour of gold nanoparticles. This attributed to the anisotropic distribution of the residual surface charge and generated electric dipole which are accountable for linear reorganization of gold nanoparticles into nanochains.[18]

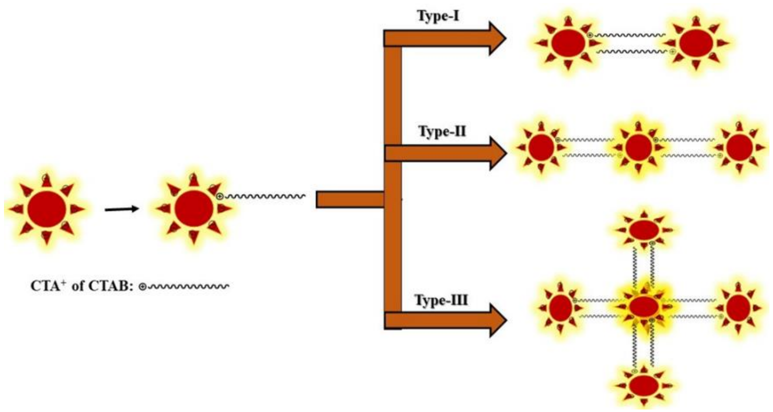

Figure 8.5: Gold nanoparticles assembly with different concentration of surfactant (CTAB).[18]

The non-ionic surfactant such as Tween 20, Tween 40, and Tween 60 could be guided the one-dimensional self-assembly of gold nanoparticles. The self-assembly process was controlled by the fine structure of the surfactants and proposed the non-uniform distribution of surfactant on the nanoparticle surface created the electric dipole-dipole interaction, responsible for directing the one-dimensional self-assembly process.[19] The cationic surfactant CTAB molecules offer steric and electrostatic repulsion between two nanoparticle if they approach each other. The two nanoparticle can be brought together by solvent evaporation. CTAB molecules can anisotropically assisted in drawing the nanoparticle together. The rate of evaporation and concentration of surfactant would be directed different two dimensional of gold nanoparticle assembly architectures.[20]

8.5 Application of Self-Assembly of Gold Nanoparticles:

The advancement of gold nanoparticle self-assembly synthesis promises next generation of technological applications including wearable sensors, photocatalysis, drug delivery, microelectronics, and medical diagnostics. The self-assembly of gold nanoparticle can acts as acceptor due to presence of delocalized electrons and can interact with electromagnetic field of the donor dipole is the major reason for physical origin of surface energy transfer. This molecular beacon with correlation between the self-assembly of gold nanoparticle with organic dye rhodamine B and the non-radiative nano-assembly surface energy transfer can be used as spectroscopic ruler or molecular ruler in probing advanced functional materials.[5]

The coupling of surface plasmon resonance of gold nanoparticles with organic dye molecules such as rhodamine 6G can results in enriched linear and non-linear optical properties such as surface enhanced Raman scattering signal. The gold nanochains could use as surface enhanced Raman scattering signal enhancer for rhodamine 6G.[16] Gold nanoparticles in sub-nanoscale can be very easily detected by fluorescence and make them a very attractive contrast material for medical diagnostics. It was anticipated that gold nanoparticles entrapped in the unilamellar block copolymer vesicles could be utilized in the imageable drug carriers, nanoreactors or nanocarriers.[21]

8.6 Conclusions and Future Perspectives:

In conclusions, the molecules guide the nanoparticle self-assembly due to interparticle interaction involved between the nanoparticle surface ligand. These self-assembly can be chemically controlled such as pH of the solution medium, ionic strength of the solution, temperature of the mixture, as well as UV light. These self-assembly of gold nanoparticle found in various application such as spectroscopic ruler, surface enhanced Raman spectroscopy, nanoplasmonics, biomedical, sensing, catalysis. The future of self-assembly of gold nanoparticle appearances diverse and bright. The synthetic strategy for self-assembly can be improved by continuous development of experimental strategy along with the theoretical framework of the surface plasmon coupling based on the spatial configuration. The further research on gold nanoparticle assembly will give rise to novel effects, exciting discoveries, and innovative next generation of technology application specially in the organic synthesis, biomedical diagnostics, wearable sensor, photocatalysis, etc.

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