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Harnessing Anisotropy in Nanoparticles: Current Strategies and Applications

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Abstract:
Nanotechnology has turned out to be a standout amongst the most encouraging advances connected in all zones of science. Anisotropic nanoparticles are a class of particles that are asymmetric in shape and have at least one dimension at nanoscale. These type of nanoparticles exhibit direction and dimension dependent chemical and physical properties. These may be composed of one or more components. Anisotropy brings features that cannot be obtained simply by tuning the size of isotropic nanoparticles. Such type of great changes in the properties of anisotropic nanoparticles makes them a good candidate for introducing a vast area of applications. This review presents a glimpse into this interesting area. We discuss the background, size, shape, synthesis methods, compositions, characterization techniques and applications of anisotropic nanoparticles.

Keywords: *Anisotropic NPs, Plasmon Resonance, Bio-sensing, Bio-imaging, Photothermal therapy, Drug Delivery.*

Introduction:

Particles that have at least on dimension less than 100nm are referred to as nanoparticles. Comparison of these particles with bulk materials yields novel properties due to larger surface area (1). Ever since the evolution of nanoparticles shape has played a major role in deciding the properties and various aspects of nanoparticles (2, 3). The simplest change that can be seen directly due to change in size and shape of nanoparticles is their colour, which arises due to confinement of electrons (4). In case of symmetric or isotropic nanoparticles, the motion of electron is same in all the dimensions and hence the properties remain almost same by tuning their size. On the contrary, asymmetric and anisotropic nanoparticles exhibit different properties along different directions due to the different type of motion of electrons in many directions. Different sort of anisotropic nanoparticles and their applications are reported in literature such as noble metal ANPs (5), semiconductor ANPs (6), Ceramic ANPs (7), Polymer ANPs (8), Metal Oxide ANPs (9), Carbon Based ANPs (10), and magnetic ANPs (11) and so on. According to Mie theory, the plasmonic peak position of a metallic nanoparticle depends on its size and shape. In symmetric nanoparticles such as spheres, this peak can be tuned in a small region of wavelength by varying the size of nanoparticle. Whereas in ANPs, the plasmonic peak can be tuned in a large region of wavelength. Also, multiple peaks can be achieved by introducing anisotropy in nanoparticles. These multiple peaks observed in absorption spectra are often extended in NIR region which is the most compatible region for studies related to tissues, hence they become a good candidate for diagnostic applications (12, 13). In case of

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

magnetic nanoparticles the coercive field of anisotropic nanoparticles is more as compared to symmetric nanoparticles (14).The applications of ceramic nanoparticles are also enhanced by introducing anisotropy in it, authors have reported increased applications of potassium hexatitanate whiskers (15), a high surface area of potassium titanate increases the ion exchange capacity (16).

In this review we will focus on anisotropic nanoparticles prepared by different synthesis methods. We will also discuss the applications specifically arising due to the anisotropy introduced and different methods to control their shape and size. Several techniques used for characterization of these particles will also be discussed.

Methods of Preparation:

Two general techniques to fabricate the NPs are top down and bottom up. In top down methods, the size is reduced by mechanical methods (17). While, the metal ions are reduced chemically to Metal NPs in bottom up method, it provides a better control on particle growth and size. A number of synthesis methods including Seed mediated synthesis, template assisted synthesis, surfactant directed synthesis, polyol assisted synthesis, biological synthesis, photochemical synthesis, electrochemical synthesis and hydrothermal synthesis etc have been developed for the synthesis of ANPs. Each method has its own merits and demerits. In the following section we will discuss these strategies of ANPs synthesis.

Seed Mediated Synthesis:

Seed mediated synthesis process is a two step process for producing nanoparticles. At first a seed is prepared by reducing a metal salt with the help of a strong reducing agent. Then these seed particles are allowed to grow in the desired shape in presence of a mild reducing agent to produce anisotropic nanoparticles. As in this method seed particles are enlarged by addition of metal atoms in many steps hence it becomes easy to control the shape of final nanoparticles. It gives the advantage of getting ANPs that have size, shape, surface and other properties dependent on the choice of seed, reducing agent and the concentration of surfactant. The second step involves the reduction of metal ions in presence of a mild reducing agent which is carried in presence of seed metal particles thus the newly formed nanoparticles try to assemble on the surface of the already present seed particles (18). The same strategy can be seen in Zsigmondy's nuclear method, which is also a two step process for producing the nanoparticles of desired morphology (19).Varying the amount of seed nanoparticles is during the synthesis results in the size variation of end product. The size of GNRs decreases as the amount of seed particles increases in the reaction. Many external molecules and ions may be used to change the growth of nanoparticles so that it may result in different morphologies. As one can obtain triangular nanoprisms of Gold by using a little amount of iodide ions while synthesizing the GNRs (20). The concentration of the surfactant or capping agent can also alter the shape of the resulting nanoparticle, as the size of the micelles varies with concentration of surfactant. Millstone et al. (21) has reported the formation of nanoprisms by reducing the gold salt using ascorbic acid in the presence of NaOH and concentrated CTAB solution by a three step process. The size of these nanoprisms can be varied by using nanoprisms as seeds in the gold solution and further reducing it by a mild reducing agent (22).Chen et al. (23) has reported the formation of Silver nanoplates with size variation of 40-300 nm by simple reduction method at room temperature in the presence of CTAB and Ag@citrate seed particles of about 15 nm, clearly indicating the dependence of size on the dilution extent of surfactant. Fan et al. (24) has synthesized Au@Pdnanocubes (core-shell structure, having Au as core and Pd as shell) using seed mediated synthesis in two steps. In this a 30 nm Au octahedral was first grown using a 3 nm Au nanosphere, and then a nanocube was grown on it by reducing H_2PdCl_4 with the help of ascorbic acid in the presence of CTAB. Many other authors have

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

also synthesized these types of core-shell bimetallic nanoparticles using the seed mediated synthesis (25, 26).

Polyol Synthesis:

The polyol synthesis for small particles started in 1989 and was first used by Fievet, Lagier and Figlarz (27). Polyols are basically alcohols having multiple hydroxyl groups. They have water comparable polarity and solubility, which enables one to use simple metal salts as starting materials during the synthesis of metal nanoparticles. They can dissolve many precursor salts easily. They have another advantage of becoming reductive at elevated temperatures, thus making them appropriate for one pot synthesis of metal nanoparticles. Many authors have reported the synthesis of ANPs using polyol method. Atmane et al. (28) has synthesized monocrystalline Co NRs of varying size by using a Co(II) dicarboxylate as precursor in the presence of BD. He has also presented an approach to control the size by using legands as a key ingredient in the synthesis. Ni NRs of diameter 11 nm and length 75 nm were synthesized using Castor oil (a natural polyol) and it was found that the morphology of the resultant ANPs depends on the precursor concentration, as its three molar concentrations resulted in NRs while six molar produced nanospheres (29).Biacchi et al. (30) has reported the synthesis of branched, triangular, nanoplates and octahedron Rhodium NPs in the presence of EG, DEG, TrEG and TEG polyols and has also shown that how proper selection of polyol solvent can manipulate the morphology of resulting NPs.Rhodium tripods of size 11 nm have also been synthesized in the presence of EG (31). Zhang et al. has reported the formation of Rhodium nanocubes of edge length 6.5 nm by a seedless polyol method using EG (32).Many other authors have synthesized Bipyramids of Pd (33),wires of Pd, PdPtBi and Ag (34,35,36), icosahedra of Pd (37), cubes of PdNi and Ag (38, 39), dendrites of PdRh (40), branches of Pt (41), flowers of Pt (42), rods of AuAg (43) and plates of BiRh (44) in the presence of polyols like EG, BD, DEG, PDO and PD etc.

Biological Synthesis:

Natural frameworks are fit for making utilitarian superstructures of inorganic nanomaterials, for example, indistinct silica, magnetite (magnetotactic microscopic organisms) and furthermore, calcite (45). In this method, shape controlled sysnthesis of nanomaterials has been accomplished either by development in compelled situations, for example, layer vesicles or through effective molecules, for example, polypeptides that bind particularly to crystallographic planes of inorganic surfaces. Microorganisms have been appeared to be vital nanofactories that hold monstrous potential as ecofriendly and practical devices, staying away from lethal, harsh synthetic compounds and the high vitality request required for physiochemical synthesis. Microorganisms can aggregate and detoxify overwhelming metals because of different reductive chemicals, which can decrease metal salts to metal nanoparticles with a tight size dissemination and, thus, less polydispersity. In the course of recent years, microorganisms, including microscopic organisms, (for example, actinomycetes), parasites, and yeasts, have been considered widely for the synthesis of nanoparticles.Anisotropic Silver Nanoparticles can be synthesized using Bhargavaeaindica (46) and Silver Nitrate. During the reaction a change in the color of the culture medium indicated the formation of Silver Nanoparticles. The same microorganism has also been used to produce Gold Nanoflowers (47). Bacillus amyloliquefaciens is another microorganism which has been reported for the synthesis of Cadmium Sulfide Nanoparticles (48). Bacillus pumilus, Bacillus persicus, and Bacillus licheniformis have been used to synthesize Triangular, Hexagonal and Spherical Silver Nanoparticles (49).

Now days, phytonanotechnology has given new roads to the combination of nanoparticles and is an ecofriendly, basic, fast, stable, and financially savvy technique.

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

Phytonanotechnology has points of interest, including biocompatibility, adaptability, and the therapeutic appropriateness of integrating nanoparticles utilizing the all inclusive dissolvable, water, as a diminishing medium (50). Panax Ginseng, which is a herbal plant have been used to synthesize silver and gold nanoparticles (51, 52, 53). Synthesis of ANPs using plants basically involves boiling the small pieces of plant's part like leaves, roots, fruits and stems with water to obtain the extract. Then this extract is filtered and centrifuged for the reduction of metal salts. Leaves of Cymbopogan citrates have been used by KadarkaraiMurugan to synthesize spherical, triangular, hexagonal and rod shaped Gold NPs by controlling the ratios of plants extract and metal salt solution (54).

Adsorbate Directed Synthesis:

In ADS, molecules are used as an adsorbate for controlling shape of the synthesized nanoparticles by selectively adsorbing to a particular plane of the crystal, which lowers the surface energy of that plane and makes that plane stabilised. Oriented Aggregation and Directed Growth are two techniques of ADS. Any addition of metal atoms directs the growth of crystal at particular planes which have weak binding of molecules in case of directed growth synthesis. However, on the other planes which have strong binding of adsorbate molecules, metal atoms do not grow in size. In an oriented aggregation mechanism, some seed particles support aggregation at certain planes by strongly binding themselves with adsorbate molecules. This method has been used to synthesize rectangular bars, octagonal rods, nanobeams(55) and nanowires(56). It is seen that when particles capped with citrate are used as seeds in a solution of CTAB in presence of Ag^{+} ions, then bipyramidal gold nanocrystals are formed. However, the same synthesis resulted in the formation of Gold nanorods when seed particles used were CTAB capped and pseudospherical in shape (56, 57). Also, CTAB capped seeds are used to synthesize cylindrical nanorods rather than non cylindricalnanorods (57, 58). Iodide ions possess the ability to suppress the crystal growth along the direction Au[111], hence an addition of these ions to growth solution results in triangular nanoprisms (59).If the growth solution contained a mixture of CTAB and BDAC (BenzylDimethylhexadecyl Ammonium Chloride), the aspect ratio of nanorods produced then was increased by a significant amount (58). MonodisperseAu@Ag and Au@Pd core shell nanocubes were obtained by the addition of octahedral gold nanocrystals as seed particles (60). However, if these octahedral Gold nanocrystals were replaced by Gold nanorods then also core shell nanoparticles having same morphology were obtained, which were transformed into hollow nanostructures by Galvanic Replacement Reactions (61). Gold nanostars can also be obtained just by adding NaOH to growth solution rapidly. These nanostars have multiple Plasmonic peaks due to their irregular structure and spikes on surface (62).

Photochemical Synthesis:

Anisotropic Nanoparticles may also be synthesized by reduction of salts through radiation process and photochemical reactions. In photochemical reactions the solvent is not needed. Also in this process the resulted nanostructures are free from any impurities and produce nanoparticles in high yield as compared to other methods. Colloidal Gold ANPs are formed when Chloroaurate solution with CTAB templates is irradiated by UV light (63). Synthesis of Anisotropic Gold Nanoparticles has been reported by Esumi et al, by irradiating chloroaurate solution with UV light while CTAB templates were present in the mixture (63). As the reducing agents are not present in this method, the growth becomes slow which is advantageous to synthesize uniform structures (64). Using 1-D templates such as DNA in place of conventional templates results in 1-D nanowires of diameters ranging from 40 nm to 80 nm (65). This method does not disturb the DNA structure and therefore it may be utilized

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

to produce composite ANPs. Crown shaped nanoparticles of Platinum have been reported by irradiating the Platinum solution having G4-NH2 PAMAM with UV light. Dendrimers used in this synthesis acts like a template to control the size of the synthesized particles (66). A change in shape and size has also been observed by illuminating the already synthesized nanoparticles with radiation, such a transformation has been reported in which Silver nanoparticles were transformed into nanotriangles (67). Nanoplates and nanostars like structures have also been synthesized by photo chemically reducing the Titanium Dioxide assisted Gold salt (68). Many bimetallic nanoparticles have also been synthesized using this method which included core-shell nanoparticles, alloy nanoparticles and nanorods of Au and Ag (69).

Surfactant Directed Synthesis:

Surfactants play a vital role in controlling the shape of nanoparticles. Among all other surfactants used for synthesis of Gold Nanorods, CTAB affects the morphology of synthesized rods to a high extent due to its hydrophobic nature. A bilayer is formed due to the self assembly of single chained CTAB in aqueous media (70). During the synthesis of nanorods, aspect ratio depends on the length of the chain also (71). Longer nanorods with a slow growth rate are synthesized when a long chained surfactant is present in the synthesis (70). A wide variety of shapes such as rectangles, cubes, stars, triangles, hexagons, dendrimers and rods may be obtained using a surfactant at room temperature (72). Cetylpyridinium Chloride is another surfactant which has been used to synthesize highly monodisperse polyhedral gold particles like cubic, octahedral and dodecahedral (73). Convex shaped polyhedrals having low catalytic activity have been reported by using CTAB and if CTAC is used in place of CTAB, concave nanocubes were formed (74,75). If Halide ion is added convex shape is changed to concave nanocubes (76). Similarly, in case of pseudospherical particles, addition of Halide ion results in nanorods or nanoprisms (77). While synthesizing Gold nanoparticles using Zwitterionic surfactant a dendritic nanostructure results which has most of the absorbance in NIR region (78).Nanoflowers may be formed by changing the pH of the synthesis or by adding lipids (79). CTAB and BDAC used in combination increase the aspect ratio of synthesized nanorods (80). A notable difference is seen in size, shape and morphology of resulted nanorods while the temperature of synthesis is changed (81).

Purification Methods:

The need of size and shape controlled anisotropic nanoparticles by wet chemical synthesis is extending the investigation for refining techniques to separate nanoparticles of different size and shapes. These strategies allow one to get highly monodisperse nanostructures. These monodispersenanoparticles are important when they need to assemble for producing longer nanostructures which are further used in many applications. The methods which are used to separate different size nanoparticles involve chromatography, electrophoresis, membrane filtration, selective precipitation, extraction and centrifugation (82).

Applications of ANPs:

Increased surface area and plasmonic properties make ANPs potential candidate for applications like targeted drug delivery, imaging, theranostics and sensing.

Biosensing:

The detection of biological agents, harmful and toxic substances is important for diagnosis and ecological observations (83). Generally, biosensing methods are based on measurements of color changes, Plasmonic shifts, scattering, absorption of UV-visible light and the properties of material like conductivity and dielectric constant (84). For these techniques the information of constituting elements is obtained by sensing based on ANPs which changes the color of solution in which it is mixed or shifts the Plasmonic band and at times enhances the

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

Raman Scattering. The scattering properties and coefficient of absorption in UV-visible range changes when biomolecules are present and the localised surface plasmon resonance band shifts. It brings a high sensitivity in optical detection and enables a better calorimetric biosensing (85). For example, longitudinal plasmon bands of AuNRs are highly sensitive for change in dielectric properties, when they are used for sensing (86). Nanorods having an aspect ratio of 3 suffered a red shift of 40nm caused by the change refractive index of the solution in the presence of the biomolecules (87). The sensitivity of detection depends on the aspect ratio of NRs (88-90). A detection limit of 0.1ng/mL for nutravidine is achieved easily by functionalising the NPs with biotin (91). A sensitivity limit of 1nm while detecting thrombin has been reported by using nuclic acid functionalised poly dispersed Pt NPs (92). Same size of nano disks and nano rings have been used by Sutherland et al to compare the dependence of Refractive Index on shape (93). In his study he has reported that sufficiently high sensitivity is exhibited by nano rings as compared to nano disks. AuNRs functionalised with alkanethiol upon coated by antibody shows multiplex sensing by easily detecting three different targets (86). DNA identification of multiple targets has been reported by Kim et al using AuNPs patterned on wire systems (94). Silica coated AuNRs when coated on quartz substrate modified with PVP, can be used as a platform for calorimetric sensing. The change in color produced by it can be observed by naked eye and the quantitative information of IgG that is present in the sample is also obtained (95). Au nano shells developed by Talley and co-workers showed sharp SERS property than Au nanospheres (96). A cholesterol biosensor has been fabricated by Wang et al using hybrid nanorods of zinc oxide functionalised with Gold or Platinum and MWCNTs (97). Locharoenrat and co-workers developed bimetallic NRs of Gold and Palladium and explained that longitudinal peak exhibited at 800-900nm shifted as a function of shell thickness and medium's dielectric property (98). Pd functionalised NRs show increased sensing limit for CO as compared to immaculate Zincoxide NRs. This improved sensing is ascribed to chemical and electronic sensitivity of PdNPs (99).

Bio imaging:

Now a day's biological imaging has gotten more noteworthy and enthusiasm for clinical practice and research. Various imaging techniques have been created to either comprehend the natural procedures in tissues, living cells and organs or identifying and evaluating the diseases for structuring a better treatment approach. Many methods from Positron Emission Tomography, Ultrasounds and Magnetic Resonance Imaging to the optical methods like Single Photon Emission CT, Computed Tomography and NIR Optical Imaging have been reported for different purpose. Out of all these techniques, Optical Imaging provides wealthy contrast mechanism while utilizing properties of light. Although the contrast agents that were used conventionally had problems like low quantum yield, poor stability in photo, less sufficient in vivo and in vitro stability and also the unnecessary interaction with cells and all these issues affect the resolution of image during application (100). For avoiding these issues, probes of many ANPs are being used now days. These probes are preferred over others as they provide good absorption, stability, brightness and biocompatibility. Intravital Microscopy involves imaging of surface cells using light of visible region (101) while NIR light is required to image tissues which are situated deeper than 500μm. Great absorber of visible light is haemoglobin that absorbs light at < 650nm and that of IR light is water which absorbs it at > 900nm. Therefore, shape and size of ANPs that is used is selected such that it shows good absorption in the region 650-900nm (102). For imaging neck and head cancer cells Kopelman et al used AuNRs coated with antibody to target cancer specific antigens in Computed Tomography (103). As reported by Huang et al cancer cells can be

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

successfully imaged by using AuNRs functionalised with anti epidermal growth factor (104). Photoacoustic tomography techniques can monitor vascular events by using NRs while using Inter Cellular Adhesion Molecule 1 functionalized AuNRs for viability of photoacoustic imaging of this molecule, Kim et al found that these images had difference in normal cells and inflamed cells, also these results were in agreement with fluorescence images (105). Coating ANPs with silica does not include any toxicity and enhances the NP uptake. Using such ANPs Gambhir et al captured images od spatial resolution 340μm and temporal resolution of 0.2s (106). Among hexapods, rods and cages, hexapods were found advantageous in a comparative study. High assembly of hexapods in cancerous cells intensifies the resolution of image and increases photothermal destruction of cancerous cells. Also in hexapods the localised Plasmonic peak can be controlled by changing the length of sides which enables the use of visible to NIR region light source (107). In two photon fluorescence imaging and optical microscopy the use of AuNRs has been reported as a contrast agent (108,109). It has also been reported that two photon fluorescence signal arising from AuNRs is 58 times stronger than that obtained using Rhodamine molecule (109,110).

Drug Delivery:

By and large, drug delivery carriers are being created with the point of accomplishing high drug assembly at the target, so they extraordinarily enhance the drug adequacy and decrease the toxicity as well as harms amid applications (111,113). As ANPs are effortlessly surface functionalised using polymer for focussing a specific cell, they are viewed as a potential possibility for drug carrier applications. Many trust that issues like actuated effects and multi drug resistance can be circumvented by using ANPs for drug delivery (114). The drug can be encased on the surface of a NP by coating these NPs with some polymers. For example, Chen et al used Gold NRs which were surface engineered for HIV treatments. Manifestation of drug coated AuNRs to NIR light actuated the delivery of DNA vaccine (115). Similarly for the treatment of RS virus a protein formulation of respiratory synctial virus fusion based on AuNR is also under progress. Premkumar et al reported the use of AuNR conjugated with doxorubicin for delivering DOX in cancer therapy. This conjugation is done by coating doxorubicin on AuNRs coated with Polystyrene Sulfonate (116). Hydrophilic and Hydrophobic drugs have also been reported to be delivered by caged AuNRs (117). Highly destructive effects under NIR region at cancerous cells and selective targeting using AuNRs conjugated with some dendrimers on its surface has been reported by Cui et al (118).

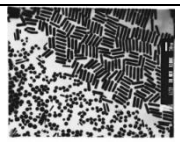
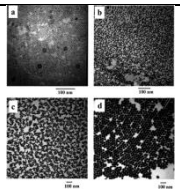
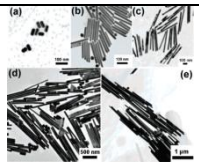
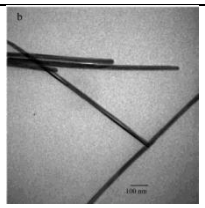
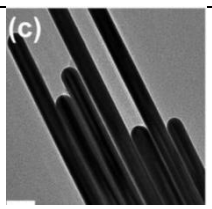
Photothermal therapy:

In photothermal therapy, cancer cells are destroyed by generating heat with photon's energy. It is a slightly invasive therapeutic method for destruction of cancerous cells (119). Photo dynamic therapy requires a photo sensitizer which generates a singlet oxygen by interacting with light to destroy cancerous cells (120, 121). Besides being used on a large scale for cancer therapy, photo dynamic therapy has shortcomings like being not very effective in case of deficiently oxygenated tumours, lacks complete selectivity and assembling photo sensitizer into tumours. Also, an unwanted photosensitivity is required to reside till the drug is eradicated (122, 123). Although authors have reported that PDT agents can be extremely restrained to tumours. PDT agents have been efficiently delivered to the target sites using PEGylated GNP conjugates (124-127). Using PEGylated GNP conjugates while delivering PGT agents adds the advantage of quenching the fluorescence of PDT agent till it is delivered at target. Using ANPs in PTT increases the effectiveness of cancer treatment (122, 123). Heat generation in PTT is increased using ANPs due to its absorption of light in NIR region and it becomes more effective. Photo thermal

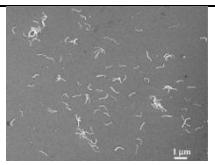
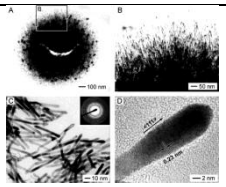
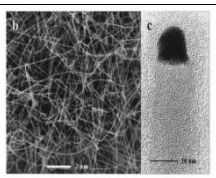
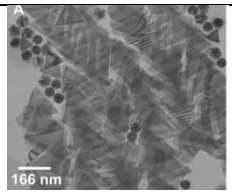
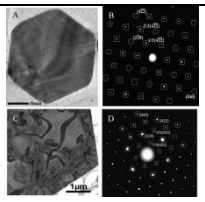
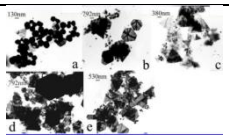
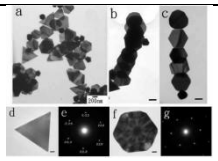
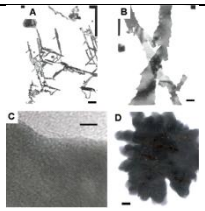
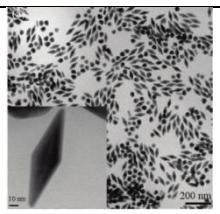
January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

therapy based on ANPs has shown better results as compared to photo dynamic therapy under the same experimental conditions (128). Normal cells are less damaged while using ANPs in Photo thermal therapy as it uses longer wavelengths (129, 130). Raviraj et al., used AuNRs coated with polyelectrolyte to show the synergistic effects of PDT and PTT. Desired effects were induced on targeted cells using LED arrays of low power without using photo sensitizer (131). Epithelial cells were treated using NRs coated with anti- EGFR monoclonal antibody by El- Sayed and co-workers. However it has been reported that malicious cells are successfully destroyed using low power light while a high power light results in death of normal cells (132). When cancerous cells were exposed to ultrasound at in-vitro condition, their internal temperature raised to 200C while that in case of in-vivo conditions raised to >450C by using Protein shell micro bubbles to encapsulate and release NRs (133). An increased efficiency has been noted while using AuNRs@Pt nanostructures for photo thermal therapy against targeted cells (132). However, coating Pt at nanostructures mildly increases cellular uptake but the longitudinal Plasmonic band becomes less sensitive while using it (134).

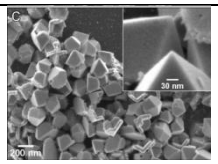
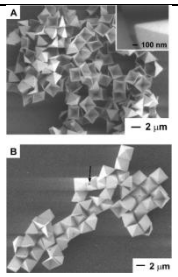
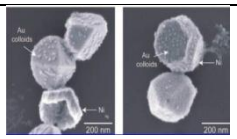
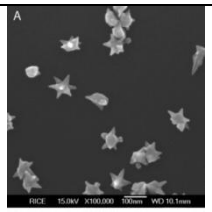
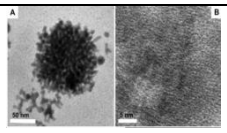
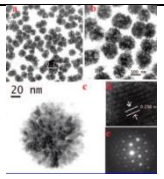
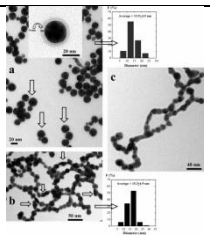
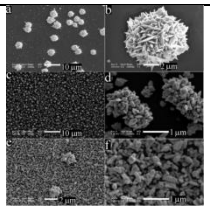
Table 1:

Composition	Preparation Method	Size and Shape	Images	Reference
Au	Electrochemical method	532, 1064nm		135
Au	Seed growth method	5-40nm		136
Au	Seed growth method	50-1700nm		137
Ag	Seedless, Surfactantless Wet Chemical Synthesis	0.15-8µm		138
Au	Chemical Synthesis	1-2µm, and 5-7µm		139

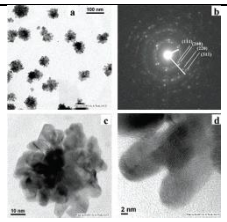
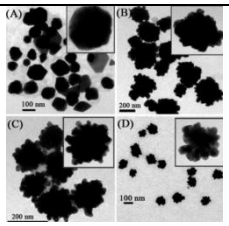
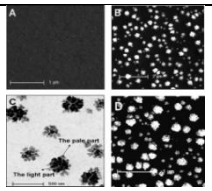
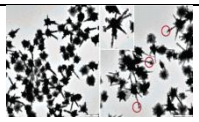
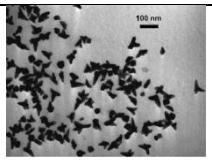
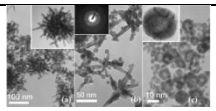
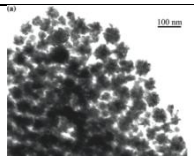
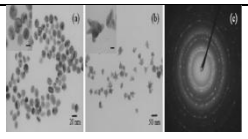
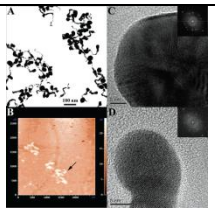
January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

Au, Pd	Chemical Synthesis	0.5-10 µm		140
Pt	Chemical Synthesis	100nm		141
Au-Si	Precipitation Method	3-15nm (Diameter)		142
Au	Chemical Synthesis			143
Au	Chemical Method	10µm		144
Au	Chemical Method	1-200nm		145
Au	Chemical Method	Width 60-500nm Thickness 6-20nm		146
Au	Chemical Method	-		147
Au	Seed-mediated approach	Length 90nm Diameter 30nm		148

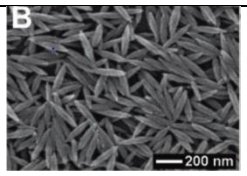
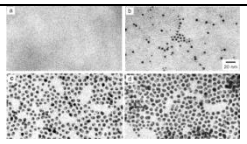
January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

Au,Ni, Si, Cr*	Top-down Method	50-150nm		149
Ni, Au	Template Assisted Synthesis	50nm		150
Au, Ni	Fabrication Method	50-200nm		151
Au	Seed growth method	100nm		152
Au	Chemical Method	3nm		153
Au	Wet Chemical Method	140-160nm		154
Au	Seed Growth Method	10-20nm		155
Au	Electrochemical Growth Method	10nm-4µm		156

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

Au	Colloidal Reduction	55-65nm		157
Au	Colloidal Reduction	80—270nm		158
Au-Pt	Wet Chemical Method	100-390nm		159
Ag, Au	Seed Growth Method	100nm		160
Au	Wet Chemical Method	30nm		161
Ag, Au	Wet Chemical Method	10-50nm		162
Au	Wet Chemical Method	37nm		163
Au	Wet Chemical Method	30-40nm		164
Au	Wet Chemical Method	5-25nm		165

January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

Au	Wet Chemical Method	320-360nm		166
CoPd	Wet Chemical Method	14nm		167

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January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

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January-February 2020
ISSN: 0193-4120 Page No. 4114- 4131

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