FORM 2

THE PATENTS ACT, 1970
(39 of 1970)
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THE PATENT RULES, 2003

PROVISIONAL SPECIFICATION

(See section 10 and rule 13)

2262 /CHE/ 2008

ORIGINAL 17 SEP 2008

TITLE OF THE INVENTION

"FACILE SYNTHESIS OF HIGHLY ANISTROPIC GOLD NANOFLOWERS: A NEW CLASS OF INFRARED ABSORBING NANOMATERIALS WITH APPLICATIONS IN LABELING AND PRINTING"

We, **INDIAN INSTITUTE OF TECHNOLOGY, MADRAS,** of IIT P. O., Chennai-600036, India;

The following specification describes the invention:

The present invention relates to a method for the synthesis of a new class of anisotropic gold nanostructures in the form of "nanoflowers" that are capable of absorbing near-infrared (NIR) and infrared (IR) radiation of the electromagnetic spectrum. Optical absorption of this material in the IR region makes these nanoflowers promising candidates for developing infrared filters. Good optical transparency of monolayers of nanoflowers-coated glass in the visible window makes the material useful in several different commercial applications. The NIR absorbing property of this material provides an opportunity for thermal therapy of tumors in deep tissues Sharp spikes on the nanoflowers would enhance the local electric field around the nanoflowers, thereby making them useful in surface enhanced Raman spectroscopy (SERS). Such SERS would be useful for ultra-trace and even single molecule detection. Biocompatibility of gold will make these materials useful in biological applications. The possibility of anchoring bioactive molecules on gold surfaces and delivering them into the skin using the sharp spikes makes these materials useful in biological applications. The inherent beauty of these materials and the possibility to visualize them with optical and other microscopies and possibility to label nanoflowers with molecules will make them useful in security inks.

Spherical nanoparticles have been the subject of intense technological research for several years. Several new advancements in the area of catalysis, molecular detection, biological delivery and SERS have happened in the past few years. Several new classes of materials such as carbon nanotubes, metallic and semiconducting nanowires and nanorods and nanotriangles or prisms have been reported.

Researches in the recent past have shown that anisotropy in the structure adds new properties into the nanosystem. Therefore, highly anisotropic systems are expected to produce numerous extraordinary properties which have not been possible for spherical nanosystems. One of the promising properties is optical absorption.

Over 49% of the solar power at sea level is due to IR radiation. A suitable and affordable material for IR absorption can therefore reduce the power requirements for air conditioning in buildings and automobiles. Harvesting this IR light for photovoltaics adds another dimension to the photovoltaic industry. The detection of low energy radiation and development of suitable devices for such application are desirable. From all these perspectives, it is important to develop materials that are or would be useful for these applications.

There are some references in the art that the applicants are aware of. They include:

(a) United States patent 20060207647-High efficiency inorganic nanorod-enhanced photovoltaic devices.

(b) WO/2007/095386-Photovoltaic device with nanostructured layers.

(c) United States patent 6685730 – Optically-absorbing nanoparticles for enhanced tissue repair.

(d) United States patent 6515749 – Sensitive and selective chemical sensor with nanostructured surfaces.

(e) WO/1999/044045 – Single molecule detection with surface-enhanced Raman scattering and applications in DNA or RNA sequencing.

The present invention describes the synthesis of a new class of gold nanostructures called "nanoflowers" and related invention of IR absorber based on this nanostructure. The high anisotropy in the shape and related intense optical absorption in the IR region of the electromagnetic spectrum makes this material useful for the construction of an IR filter. It allows major part of the visible light to be transmitted, thus maintaining transparency. The IR absorbing property of this material allows this material for photothermal therapy. Because of the high penetration power of the IR radiation through the tissue, the tissue containing nanoflowers could absorb IR radiation better and destruction of the targeted cells occurs by the generation of localized heat. In that perspective, this material is useful for the NIR thermal therapy of tumors. The nanoflower can be targeted to the cells by appropriate antibody tagging. Biocompatibility of gold will be useful in this application. This material will also be useful for making photovoltaic devices. The nanoflower described in this embodiment will harvest visible and IR photons from the solar spectrum resulting in higher conversion efficiency.

Even though the interesting properties of anisotropic nanostructures such as NIR absorption and high SERS activity are known, high yield synthesis devoid of other contaminating structures is quite difficult. Our synthetic approach provides a method for making uniform and highly anisotropic nanostructures called nanoflower. The high SERS activity and NIR-IR absorbing property exhibited by the nanoflower make them good candidates for large number of applications in diverse areas.

The NIR-IR absorbing property of this material provides an opportunity for the development of infrared filters, photothermal therapy of tumors, photovoltaics etc. It has been recognized that the NIR-absorbing films based on gold can be used as an alternative to reflective coatings for blocking IR radiation (X, Xu, M. Stevens, M. B. Cortie, *Chem. Mater. 2004, 16*,2259). The gold-based approaches rely on efficiency and are economically viable compared to the other methods. In high temperature regions, nanoflower coated windows can reduce the temperature rise within enclosed rooms, thereby reduce the expenditure on power used for air conditioning. Preliminary studies in this direction shows that a bilayer of nanoflower –coated glass can absorb a considerable amount of heat from sunlight and can decrease the temperature of an enclosure covered by it by 4.5°C compared to that with an uncoated glass.

This material would be useful for making SERS sensors for detection and study of biologically relevant molecules, explosives, DNA, RNA and even single molecules. A large number of sharp spikes on the nanoflowers would enhance the local electric field around the nanoflowers, thereby the SERS activity will enhanced. A well-ordered, patterned substrate of nanoflowers would be able to make devices, capable of reliable and reproducible detection of single molecules. This possibility opens up new potentials for the diction ofdangerious explosives such as trinitrotoluene (TNT).

The synthesis of gold nanoflower starats from an oligoaniline capped AU nanoparticles synthesized as per our earlier report (Sajanlal, P.R.; Sreeprasad, T.S.; Nair, A.S.; Pradeep, T. *Langmuir* 2008, ASAP (10.1021/LA703593C)). These are raspberry like aggregates of AU/oligoaniline. Subsequent growth of these nanoparticles at 80°C in presence of the growth solution containing a mixture of cetyltrimethylammonium bromide (CTAB), Au^{3+}, $AgNO_3$ and ascorbic acid, which were used for the synthesis of gold naorods (Sau, T.K., Murphy, C. J. *Langmui,* 2004, *20,* 6414) resulted in the formation of gold nanoflower. One of the major advantages of the current synthesis is high yield and monodispersity of the materials formed. Almost all the nanostructures formed after the reaction had the same morphology and shape. This does not occur usually in normal synthetic protocols of standard nanomaterials. There will always be a few spherical and other shapes. The sample was centrifuged at 4000rpm in order to remove excess CTAB. The nanoflowers settled at the bottom as a sand-like precipitate.

The method according to this invention for the making of IR absorbing films involved the steps of making the nanoflowers in solution, their purification and the fabrication of a monolayer assembly of the nanoflowers on silanized glass substrate and subsequent evaluation of the optical absorption property of this layer for the development of IR filters and SERS sensors. The optical absorption measurements were done using a UV-vis-NIR spectrophotometer and SERS properties were studies using a Raman spectrometer.

Description of the nanoflower synthesis

In a typical synthesis of gold nanoflower, a growth solution which contains 20 ml of CTAB (100mM), 335μl of Au^{3+} (25mM), 125μl of $AgNO_3$ (10 mM) and 135 μl of ascorbic acid (100mM) was taken in a round bottom flask. To this solution, 2ml of the as prepared Au/Oligoaniline nanoparticles, as per the reported procedure (Sajanlal, P.R.; Sreeprasad, T.S.; Nair, A.S.; Pradeep, T. *Langmuir* 2008, ASAP (10.1021/LA703593C)) were added. It is then maintained at a temperature of 80^{0}C for 1 h. The resultant solution was centrifuged at 4000 rpm for 5 min. The residue was redispersed in water and again centrifuged for 5 min. Finally the solid redispersed in deionized water and characterized. The size of these s could be varied from 0.5μm to 10μm depending on the reaction It was observed that the size of these nanoflowers decreased by the excess seed into the growth solution.

n the scanning electron microscopic (SEM) image it was found that this material have a flower-like morphology. Figure 1 shows the large area SEM image of the nanoflowers synthesized according to the above mentioned procedure. Corresponding SEM image of a single nanoflower is shown in Figure 1B. Each nanoflower is made of a large number of stems and each stem has an unusual pentagonal symmetry. A view from the top of each stem resembles a hierarchal pyramid of stars. Inset of Figure 1B shows such a view of a single stem from the top. Each stem looks like the stacking of star-shaped plates one over other, leading the formation of a hierarchal pyramid of stars.

These are biomimetic nanostructures, which look like plant aloe vera or pineapple. These are highly irregular structures. The ridges along corners of the stems are bearing a resemblance to the cactus plant. Such a structure may alternately be called as nanostars, nanourchins, nanothorns, etc.

Figure 1. (A) Large area SEM image of gold nanoflowers. (B) A single gold nanoflower. Inset of B shows a view from the top of a single stem of a nanoflower.

Description of the nanoflower monolayer synthesized

Thin glass slides were thoroughly cleaned and functionalized with aminopropyltrimethoxysilane (APTMS) as per a reported procedure (Cheng, W.L.; Dong, S.J.; Wang, E.K. *Anal.Chem.* 2002, *74,* 3599). These glass slides were immersed in a suspention of gold nanoflowers in water, which were purified by the repeated washing with water and methanol, for 1 h (see Figure 2). After 1h, the glass slide washed 2-3 times with distilled water in order to remove the physisorbed nanoflowers and dried under a stream of nitrogen. The optical absorption spectrum of the monolayer coated glass slides was measured using Varian Cary 5E UV-vis-NIR spectrophotometer.

Figure 2. Schematic representation of the method used for the immobilization of gold nanoflowers on glass substrate and subsequent IR absorption property.

IR absorption of monolayers of gold nanoflowers-coated glass substrate

UV-Vis-NIR measurements of these materials were done using a Varian 5E spectrometer in the range of 200-2500nm. The nanoflower coated glass plate looks slightly yellowish in color and showed good optical transparency. Before taking the spectrum, the baseline measurements were carried out using two blank glass plates of the same kind which was used for the immobilization of the nanoflowers. Blank glass plates were kept in the reference as well as sample compartments of the spectrophotometer and the baseline was collected. The baseline was subtracted in the subsequent measurement in order to avoid the absorption due to the base glass slides.

UV-Vis NIR spectrum recorded from the monolayer of nanoflower-coated glass substrate (Figure 3) exhibits very strong absorption in the NIR-IR region whereas the absorption due to blank glass plate at these areas was negligible. The smaller nanoflowers of size 0.5-1 μm showed an absorption maximum around 1400nm. So, it is possible to tune the absorption maximum by changing the size of the nanoflowers.

Figure 3. UV-Vis-NIR absorption spectra of monolayers of gold nanoflowers of different size on glass substrate.

SERS based sensors using gold nanoflower

The gold naloflowers synthesized were purified by repeted washing with distilled water followed by methanol in order to remove all the unwanted materials. It is then redispersed in water. The SERS activity of this nanostructure was checked with the crystal violet molecule adsorbed on it. For the SERS measurements, the monolayer of nanoflower-coated substrate along with 10μl of crystal violet (CV) solution of different concentration was mounted on the sample stage of a confocal Raman microscope (CRM). The spectra were collected by the excitation of the sample with 514.5nm Ar ion laser. The back-scattered light was collected by a 60X objective. The signals were then dispersed using a 1800 grooves/mm grating and the dispersed light was collected by a Peltier cooled charge coupled device (CCD). Data from liquid droplets were collected with a liquid immersion objective.

The SERS spectra at various concentrations of CV adsorbed on gold nanoflowers are shown in Figure 4. In a typical experiment, 10 μl of CV solution of various concentrations was drop-casted on the monolayer of gold nanoflowers-coated glass substrate. Even at a concentration of 10^{-10} M CV, this material showed distinch spectral features of CV. But in the cas3e of a blank glass plate, even at a concentration of 10^{-6} M CV on blank glass surface, (B) 10 μl of 10^{-8} M CV on nanoflower-coated glass surface, (C) 10 μL of 10^{-9} M CV on nanoflower-coated glass surface and (D) 10 μL of 10^{-10} M CV on nanoflower-coated glass surface.

Figure 4. Raman spectra collected from (A) 10^{-6} M CV on blank glass surface, (B) 10μL of 10^{-8} M CV on nanoflower-coated glass surface, (C) 10 μL of 10^{-10} M CV on nanoflower-coated glass surface.

The nanoflower showed high SERS enhancement factor of the order of 10^9. The high SERS activity exhibited by the nanoflowers can be made use of for a rapid and accurate detection of biological species and explosives such as TNT.

Because of the unique morphology of the nanoflowers, this can be used for security printing, labeling, paintings, etc.

The present invention provides a new variety of anisotropic nanostructures called nanoflowers with unique structure which exhibits good NIR-IR absorbing property and high SERS activity. It is necessary to have uniform size and shape to the nanoparticles to make reliable and reproducible nanoparticle based devices. It is hard to synthesize uniform anisotropic nanoparticles with high yield without spherical and other particles. We could synthesize highly anisotropic nanostructures using seed-mediated approach in high yield with our unique seed particles. High yield, complex morphology, uniformity and easiness in the synthetic procedure make our new material and method novel. These highly anisotropic nanoflowers open up a large number of possibilities in diverse areas of science and technology.

The discovery involves the utilization of specific seed particles for the growth of nanomaterials of definite shape and symmetry having applications in infrared absorption, photothermal therapy, surface enhance Raman, security printing etc. Anisotropic structures are fascinating because of their immediate applications in diverse areas. The idea behind our present invention is mainly based on our own paper published in Langmuir (P.R. Sajanlal, T.S. Sreeprasad, A. S. Nair,

T. Pradeep, *Langmuir* **2008**, *24*, 4607). The paper deals with the synthesis of various anisotropic nanostructures from Au/oligoaniline nanoparticles. From detailed investigation of these Au/oligoaniline nanoparticles we found they are spherical aggregates of smaller nanoparticles embedded in oligoaniline matrix which is having large number of nucleation sites. From these observations we realized that these nanoparticles can act as a seeds nanoparticle in the well established seed mediated growth method and can grow into anisotropic nanostructures. We optimized the reaction conditions to yield uniform nanoflowers in high yield.

The method of the invention involves making gold nanoflowers with high uniformity and monodispersity, involving the steps of making oligoaniline protected gold nanoparticles and their subsequent growth with a growth solution containing CTAB, Au^{3+}, $AgNO_3$ and ascorbic acid in the required ratio, in variable sizes in the range of 0.1-10 micrometer, with well defined morophology consisting of several stems with pentagonal symmetry. These nanoflowers may be coated with organic molecules, biomolecules and polymers.

Apart from gold, nanoflowers can also be made of several other metals such as gold, silver, copper, platinum and palladium, or any alloy of a combination of such metals. The nanoflower is a core-shell structure of combination of metals mentioned above and can be synthesized at practically any temperature. The method involves the use of seed particles made of gold or other metals or alloys. The growth solution comprises of all types of surfactant molecules and all kind of polymers instead of the CTAB, and all metals or non-metal ions of various oxidation states such as Ni^{2+}, Fe^{2+}, Fe^{3+}, Cd^{2+}, etc. instead of Ag.

The seed particles used in the synthesis of nanoflowers comprises of oligomers and polymers of aniline or substituted anilines or of any other organic molecule that would be suitable for this purpose. It has been seen that the gold nanoflowers obtained by the method of the invention are capable of formation into an infrared absorbing material capable of absorbing NIR-IR light from all light sources and nanoflowers of these kind coated with organic molecules, biomolecules and polymers. The nanoflowers can be coated with any organic molecules and polymers.

The infrared absorber is useful as an infrared filter, wherein the monolayer or multilayer of nanoflower on glass plates of all thickness absorbs NIR-IR radiation from all sources of light. The infrared filter may be a composite with polymers, glasses, oxides, etc where one of the constituents is nanoflowers of the invention. In the infrared filter made of the infrared absorber, the monolayer or multilayer of the nanoflower is prepared on any substrate such as glass, indium tin oxide coated conducting glass, fluoride doped conducting glass, etc. The filter made of the infrared absorber comprises two substrates transparent to visible light, wherein the infrared absorber of the IR absorber is interposed between these two substrates.

The infrared absorber is capable of use for the localized delivery of heat into the tissues by the absorption of NIR-IR radiation from all sources of light and thereof for the repair of tissues, such as for therapies based on localized hyperthermia. The IR absorber is also useful for application of cosmetics. In addition, the IR absorbers are capable of modification on the surface of the nanoflowers with molecules for better infrared absorption as well as directed delivery into tissues and organs. Other applications include as a photovoltaic device comprising, photoactive layer of gold nanoflowers exhibiting substantial absorption of radiation in the NIR-IR region of the solar spectrum, optionally supported on a substrate.

Further applications include as SERS based sensors for the detection of bio-molecules, explosives, DNA and RNA. The nanoflowers can also form the basis for diagnostic strips based on properties such as SERS, metal-enhanced fluorescence and detection of antigens immobilized on gold nanoflower by the interaction of antibodies. A diagnostic chip made of nanoflowers of the invention is synthesized as described above and the metal or alloy size is in the range of 0.1 to 10 micrometer. The nanoflowers may be coated with any organic molecules and polymers.

The nanoflowers may also be used to form a composite ink used for printing, labeling, painting etc. Of particular interest is security printing wherein the property of interest is improving the security of the product by using one of the properties of the nanoflowers. The nanoflowers of the invention are also useful in biology, medicines, therapeutics, diagnosis, security printing, infrared and optical absorption sensing, photovoltaic, etc.

Work is still underway to complete the invention. The above disclosure is illustrative and modifications and variations are possible without departing from the spirit and scope of the invention.

Dated 16th day of September 2008.

G. NATARAJ
Subramaniam, Nataraj & Associates
Agents for the Applicants

We Claim: CLEAN COPY

1. A process for synthesis of metallic anisotropic mesostructures with high uniformity and monodispersity in the form of "nanoflowers" or "mesoflowers" with size in the range of 1-2 micrometer capable of absorbing near-infrared (NIR) and infrared (IR) radiation of the electromagnetic spectrum, the steps comprising:
   (i) preparing a growth solution containing cetyltrimethylammonium bromide (CTAB), Au^{3+}, $AgNO_3$ and ascorbic acid;
   (ii) adding metal/oligoaniline seed particles to the said growth solution and maintaining the mixture at a temperature in the range of 40-100°C;
   (iii) centrifuging the resultant solution to obtain the metallic anisotropic mesostructures

   wherein the synthesized mesostructures have well defined morphology consisting of large stems with each stem having pentagonal symmetry and looks like the stacking of star-shaped plates one over other, leading the formation of a hierarchal pyramid of stars as a precipitate of length 0.1-10 μm.
2. The process as claimed in claim 1, wherein the growth solution consists of cetyltrimethylammonium bromide (CTAB) in the range of 10 to 100mL in the concentration of 0.01 to 1.00 M.
3. The process as claimed in claim 2, wherein cetyltrimethylammonium bromide (CTAB) is in the amount of 20 mL of 100 mM solution.
4. The process as claimed in claim 1, wherein the growth solution consists of Au^{3+} in the range of 100 to 1000 μL in the concentration of 10 to 1000 mM.
5. The process as claimed in claim 4, wherein Au^{3+} is in the amount of 335 μL of 100 mM solution.
6. The process as claimed in claim 1, wherein the growth solution consists of $AgNO_3$ in the range of 125 to 500 μL in the concentration of 5 to 100 mM.
7. The process as claimed in claim 6, wherein $AgNO_3$ is in the amount of 335 μL of 100 mM solution and 125 μL of 10 mM solution.
8. The process as claimed in claim 1, wherein the growth solution consists of ascorbic acid (A.A) in the range of 100 to 1000 μL in the concentration of 10 to 1000 mM.
9. The process as claimed in claim 8, wherein ascorbic acid is in the amount of 135 μL of 100 mM solution.

10. The process as claimed in claim 1, wherein the metal/oligoaniline seed particles are added in the amount of 1 to 10 mL.
11. The process as claimed in claim 10, wherein metal/oligoaniline seed particle is in the amount of 2 mL to get nanoflowers of length 0.1-10 µm.
12. The process as claimed in claim 1, wherein the metallic mesostructures are produced from metals selected from the group consisting of gold, silver, copper, platinum, palladium and any alloy or mixtures thereof.
13. The process as claimed in claim 12, wherein the metal is gold.
14. The process as claimed in claim 12, wherein the mesostructures is a core-shell structure of combination of metals.
15. The process as claimed in claims 12-14, wherein gold mesostructures are further treated with platinum or silver salts in the presence of ascorbic acid to produce bimetallic structures.
16. The process as claimed in claim 1, wherein the mesostructures are synthesized at a temperature ranging from 60 -90°C and precisely at 80°C, for a time ranging from 2 min to 3 h.
17. The process as claimed in claim 1, wherein centrifugation is done at 2000 to 4000 rpm for 5 to 10 minutes.
18. The process as claimed in claim 1, wherein the said growth solution consists of the surfactant molecules including cetyltrimethylammonium chloride cetyltriethylammonium bromide.
19. The process as claimed in claim 1, wherein the said seed particles consists of oligomers and polymers of aniline, ortho, meta and para toludines, ortho, meta and para ethyl aniline, N-methylaniline, N-ethylaniline, N-phenylethanolamine.
20. The process as claimed in claim 1, wherein the monolayer or multilayer of nanoflowers immobilized on one or more substrates selected from glass, indium tin oxide coated conducting glass, fluoride doped conducting glass and glass plates of all thickness transparent to visible light absorb NIR-IR light from all light sources.

Dated at Chennai this Nov 29, 2018

Signature:

D. Moses Jeyakaran
Advocate & Patent Agent
IN/PA — 369

ABSTRACT

"SYNTHESIS OF HIGHLY ANISOTROPIC METALLIC MESOSTRUCTURES"

The present invention relates to a process for synthesis of metallic anisotropic mesostructures with high uniformity and monodispersity with size in the range of 1-2 micrometer, the steps comprising: preparing a growth solution containing cetyltrimethylammonium bromide (CTAB), Au^{3+}, $AgNO_3$ and ascorbic acid; adding metal/oligoaniline seed particles to the said growth solution and maintaining the mixture at a temperature in the range of 40-100°C; and centrifuging the resultant solution to obtain the metallic anisotropic mesostructures with well defined morphology consisting of several stems with pentagonal symmetry as a precipitate of length 0.1-10 μm. The present invention also relates to metallic anisotropic mesostructure with high uniformity of shape and size and monodispersity with size in the range of 1-2 micrometer having large number of stems with each stem having an unusual pentagonal symmetry, wherein each stem looks like the stacking of star-shaped plates one over other, leading the formation of a hierarchal pyramid of stars.

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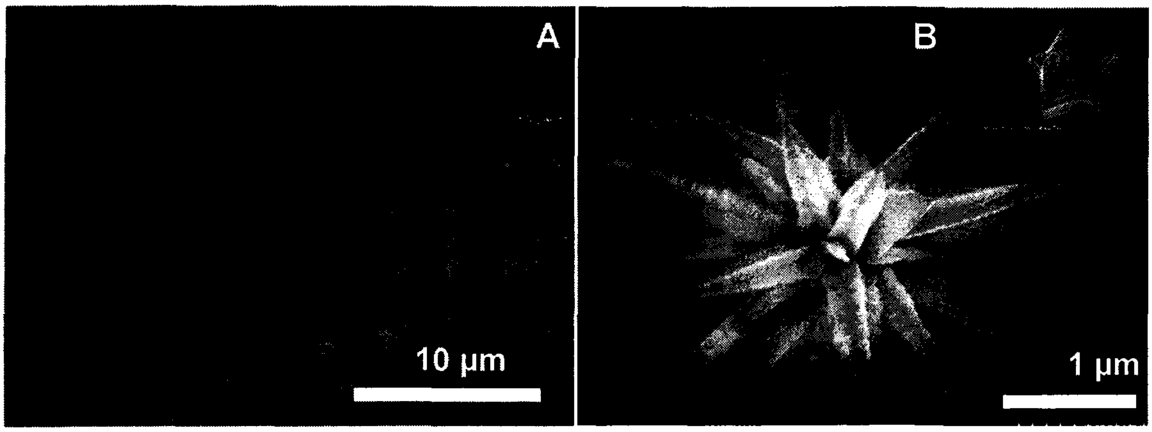

Figure 1: (A) Large area SEM image of gold nanoflowers. (B) A single gold nanoflower. Inset of B shows the view from the top of a single stem of the nanoflower. Details of the structure are visible in Figure B.

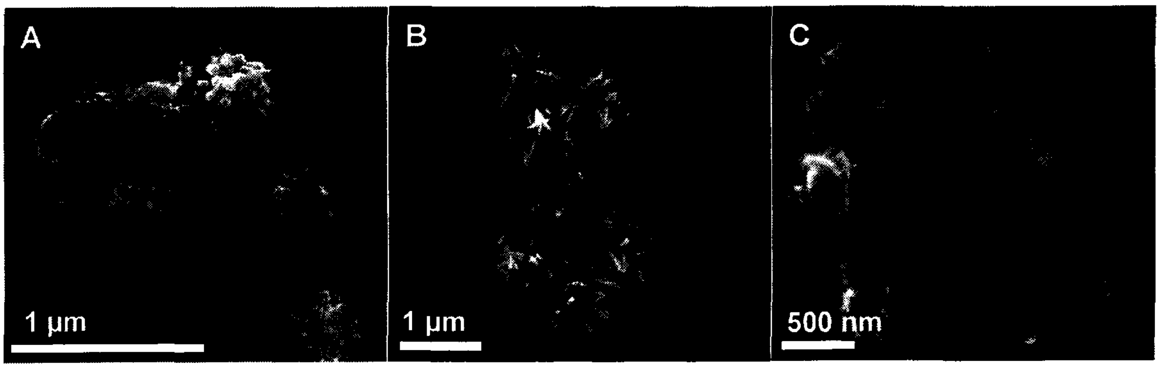

Figure 2: SEM images of nanostructures formed at various experimental conditions. (A) Meat-ball like nanoparticles formed at ice cold temperature. (B) Smaller nanoflowers (0.5 – 1 µm) formed when 5 mL of the seed nanoparticles were added into 20 mL of the growth solution. (C) Nanoflowers formed when 100 µL of Ag^+ was used in 20 mL of the growth solution

(G. NATARAJ)
of SUBRAMANIAM, NATARAJ & ASSOCIATES
Attorneys for the Applicants

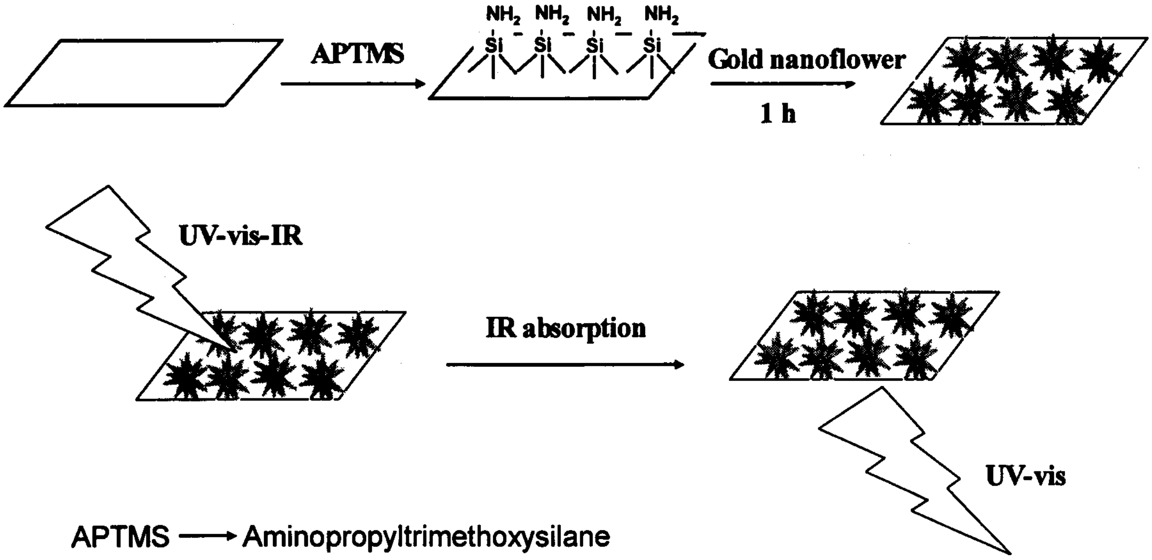

Figure 3: Schematic representation of the method used for the immobilization of gold nanoflower on glass substrate and subsequent IR absorption property.

(G. NATARAJ)
of SUBRAMANIAM, NATARAJ & ASSOCIATES
Attorneys for the Applicants

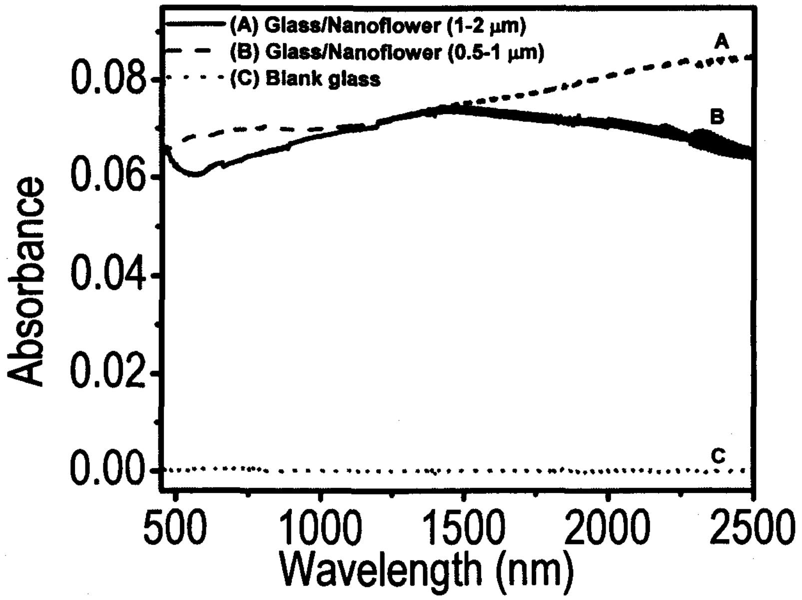

Figure 4: UV-vis-NIR absorption spectra of monolayers of gold nanoflowers of different sizes on glass substrate.

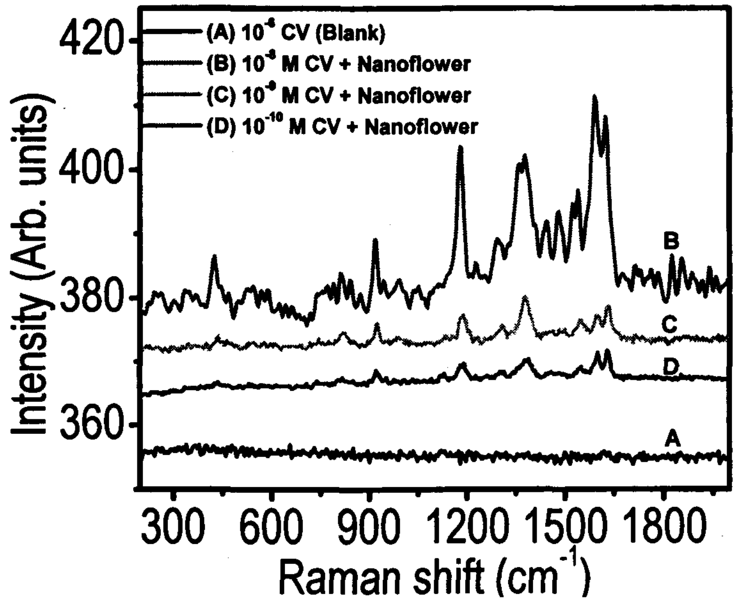

Figure 5: Raman spectra collected from (A) 10^{-6} M CV on blank glass surface, (B) 10 μL of 10^{-8} M CV on nanoflower-coated glass surface, (C) 10 μL of 10^{-9} M CV on nanoflower-coated glass surface and (D) 10 μL of 10^{-10} M CV on nanoflower-coated glass surface.

(G. NATARAJ)
of SUBRAMANIAM, NATARAJ & ASSOCIATES
Attorneys for the Applicants