CHAPTER 1

Gold Nanorods: An Overview

1.1. An Introduction to Anisotropic Nanomaterials

One dimensional (1-D) nanostructures are a class of low dimensional anisotropic nanomaterials having diameter in the nanometer range (<100 nm) and longitudinal dimension ranging from nanometer to micrometer.\(^1\) Such 1-D nanostructures having varying aspect ratios (length over diameter) possess wide range of potential applications as plasmonic waveguides and interconnectors in nanoscale devices for efficient transport of electrons.\(^2\) Often nanoparticles develop a spherical morphology to minimize their surface energy, since sphere represents the smallest surface for a given volume. However, by controlling interfacial tension it is possible to grow nanomaterials having various shapes, tailored for specific optoelectronic applications. A few examples on the design of 1-D nanomaterials have been reported recently which include metal,\(^3-5\) semiconductor\(^6\) and metal oxide nanorods.\(^7,8\)

Gold in its nanometric dimension possesses shape dependent optical and electrical properties (Figure 1.1). The optical response of spherical gold
nanoparticles exhibit a single absorption band at around 520 nm, attributed to the collective dipolar oscillation (surface plasmon resonance). However, the classical electrostatic model predicts that the nanorods of gold and silver split the dipolar resonance into two surface plasmon bands wherein the induced dipole oscillates along the transverse and longitudinal axes. A strong dependence was observed on the longitudinal surface plasmon maximum by varying the aspect ratio, while the position of transverse surface plasmon remains more or less unaffected. Gold nanorods possess more interesting optical properties compared to nanospheres: intense tunable longitudinal plasmon absorption, enhanced photoluminescence, large surface enhanced Raman cross-sections and photothermal effects. These unique properties offer a wide range of possibilities in material science and biology (vide infra). Several strategies have been adopted for the synthesis of Au nanorods and a brief summary is presented below.

**Figure 1.1.** Transmission electron microscopic images of (A) spherical gold nanoparticles with an average diameter of 48 nm and (B) gold nanorods with a mean aspect ratio of 3.3. (Adapted from reference 3b)
1.2. Synthesis of Gold Nanorods

Generally, rod-shaped metal nanostructures are synthesized either in rigid templates or in the presence of surfactants. In the former case, the metal ions are reduced inside cylindrical pores of oxide or polymeric membranes, usually called ‘hard template synthesis’.\textsuperscript{11} In the latter method, neutral or charged surfactants are used for growing nanorods, usually known as ‘soft template synthesis’ by adopting electrochemical, photochemical or seed mediated methods.\textsuperscript{16-20}

1.2.1. Hard Template Synthesis

The synthesis of metal nanorods such as Ag, Pt, Cu, Au and Ni of varying dimensions has been achieved by adopting a hard template method. These metals were deposited in the pores of the template membrane by either electrochemical or chemical (‘electroless’) reduction of the appropriate metal ion. The electrochemical deposition is accomplished by coating one face of the membrane with a metal film, which forms cathode for electroplating. Electron micrographs of aluminum template membrane used for synthesizing nanofibrils are shown in Figure 1.2. The optical properties of nanorods are dependent on their aspect ratio.\textsuperscript{12} The length of Au nanofibrils were controlled by varying the amount of metal deposited whereas depositing a small amount of metal, short squat fibrils were obtained. Alternatively by depositing large quantities of metal, long needle like fibrils can be prepared.\textsuperscript{13}
To conduct electroless deposition of metal within the pores of the template membrane, a catalyst must be applied to the pore walls.\textsuperscript{14} As a result, metal tubules are obtained in short deposition times and these tubules close up to form solid metal fibrils at longer deposition times. Unlike the electrochemical method, where the length of the metal fibril can be controlled, the electroless method yields fibrils or tubules that run the complete width of the template membrane. Recently, Huber et al.\textsuperscript{15} have described an alternative template method that entails injection of the metal melt into the pores of a template membrane.

Figure 1.2. (A) Electron micrographs of alumina template membrane and (B) Transmission electron micrograph of a microtomed section of the template membrane showing 70 nm diameter Au nanorods within the pores. (Adapted from reference 11a)

\subsection*{1.2.2. Electrochemical Method}

Gold nanorods, in high yields, have been successfully synthesized \textit{via} an electrochemical method by Chris Wang and coworkers in 1997 and this procedure allows the preparation of Au nanorods having varying aspect ratios.\textsuperscript{16} Authors have developed an approach for controlling the growth by introducing a ‘shape-
inducing reagent into the electrochemical system in which appropriate surfactants were employed as both the supporting electrolyte and the stabilizer for Au nanorods.

Typically gold nanorods were prepared via electrochemical oxidation/reduction, within two-electrode type cell (Figure 1.3). The cell consists of gold and platinum electrodes as anode and cathode, respectively. An additional silver plate is placed behind the Pt electrode. A hydrophilic cationic surfactant namely cetyltrimethylammonium bromide (CTAB), and a hydrophobic cationic co-surfactant, (tetradecylammonium bromide or tetraoctylammonium bromide) were used as electrolytes. The ratio between these surfactants controls the average aspect ratio of the gold nanorods. The electrolysis was carried out for 45 min with an applied current of 5 mA at a temperature of 42 °C, under constant ultrasonication. Au nanorods thus prepared were separated from spherical nanoparticles by centrifugation. Since the electrochemical method involves complicated experimental conditions such as sonication and constant current electrolysis, it is difficult to improve the uniformity of nanorods. Later El-Sayed and coworkers modified this procedure to reduce the formation of irregular shaped particles along with nanorods.17
Chapter 1 – Gold Nanorods: An Overview

1.2.3. Seed-Mediated Growth Method

Seed-mediated synthesis of gold nanorods were developed by Murphy and coworkers through a multistep growth process, by involving surfactant directed growth of nanorods from spherical seeds.\textsuperscript{4b,18} Seeds were prepared by reducing a metal salt in the presence of a strong reducing agent followed by the addition of more metal salts to the seed solution, along with a weak reducing agent and a surfactant. The aspect ratio of the nanorods can be controlled by varying the ratio of seed to metal salt as well as the time delay between various steps of the synthesis; however, the yields are low (Figure 1.4). More recently, same group have reported an improved synthetic procedure in which different volume of Au seeds were added to a growth solution containing a small amount of silver ions. In

![Figure 1.3. Schematic diagram of the setup for preparation of Au nanorods. The electrochemical system contains the following: VA, power supply; G, glassware electrochemical cell; T, teflon spacer and the electrode holder; S, electrolytic solution; U, ultrasonic cleaner; A, anode (Au); C, cathode (Pt). (Adapted from reference 21)](image-url)
general, the addition of low concentration of seeds produces higher aspect ratio nanorods.  

![Figure 1.4](image1.png)

**Figure 1.4.** TEM images of various Au nanorods prepared through seed mediated synthesis (A) 4.6 aspect ratio, (B) shape separated 13 aspect ratio gold nanorods, and (C) shape-separated 18 aspect ratio gold nanorods. The scale bar (100 nm) applies to all three images. (*Adapted from reference 18*)

### 1.2.4. Photochemical Method

Yang and coworkers synthesized gold nanorods by photochemically reducing gold ions in an aqueous micellar solution. The aspect ratio of the rods were controlled by varying the concentration of silver ions (Figure 1.5). This synthetic process yielded uniform nanorods, and more importantly useful in resolving the growth mechanism of anisotropic metal nanoparticles due to its simplicity and the relatively slow growth rate of the nanorods.
Chapter 1 – Gold Nanorods: An Overview

1.2.5. Other Methods

Various other procedures reported for Au nanorods synthesis include combined chemical-photochemical processes, solid support growth and bio-reduction process. Yamada and co-workers have suggested a combined chemical-photochemical method, which can accelerate the rate of nanorod formation. This method suggests the addition of ascorbic acid prior to UV light irradiation, which reduces Au$^{III}$ to Au$^{I}$. The reagent conditions are similar to that of photochemical method, except the absence of tetratodecylammonium bromide (TDAB). Addition of a dilute solution of ascorbic acid to tetrachloroaurate-CTAB mixture resulted in the instantaneous color change of the solution from pale yellow.
to colorless. Further the irradiation of the reaction mixture using ultraviolet light in a thin quartz cell resulted in the formation of gold nanorods.

Markovich and co-workers reported seed-mediated method for the growth of gold nanorods directly on mica surfaces without using silver nitrate.\textsuperscript{23a} Spherical seed nanoparticles were attached on mica surface, which was further dipped in a surfactant growth solution. Interestingly around 15\% of the surface-bound seeds are found to grow as nanorods. The yield enhancement of nanorods, compared to that obtained for the solution growth technique,\textsuperscript{18} was attributed to a change in the probability of the growing seeds to develop twinning defects. More recently, Wei and coworkers have utilized this method to grow nanorods directly on glass surfaces.\textsuperscript{23b} They studied the influence of the linker used to attach the seed particles and the concentration of Au\textsuperscript{III} ions on the gold nanostructure formation.

Gold nanorods produced through the bio-reduction process using biomass particles of alfalfa (Medicago Sativa) tend to show twins appearing either as bands or concentric forms, generating a type of nanorods based on a decahedral structure.\textsuperscript{24} The washed and milled fresh alfalfa was dried in a muffle at 95 °C for one week. The dried material was milled sufficiently to produce a fine powder and which was further washed with acid solution to remove any residues and the soluble biomolecules that may interact with gold ions. The nanorods obtained by reducing Au\textsuperscript{III} ions were found to be twinned with long axis [112] direction. The
twins appear to be parallel-bands or concentric shapes forming pentagonal nanorods. The selective separation of nanorods is the major limitation of various methods described above.

1.3. Characterization of Gold Nanorods

Crystal structure and shape of gold nanorods were studied using high-resolution transmission electron microscopy (HRTEM) and selective area electron diffraction (SAED) techniques. El-Sayed and coworkers have characterized the crystal structure of two types of electrochemically synthesized Au nanorods having short and long aspect ratios. Au nanorods of short aspect ratios (3-7) are mainly enclosed by \{100\} and \{110\} facets with an axial growth direction of [001] (Figure 1.6). In contrast, the Au nanorods with large aspect ratios (20-35) are dominated by \{111\} and \{110\} facets and their growth axial direction is [112]. In addition to the relatively stable \{110\} and \{111\} facets, the gold nanorods have large \{110\} facets with high surface energy, a unique feature of Au nanorods which is absent in Au spherical particles.

By adopting electron microscopy and diffraction techniques, Murphy and coworkers have determined the structure of gold nanorods prepared by seed-mediated synthesis, at various stages of the growth. Images of mature nanorods showed super-positions of two specific pairs of crystallographic zones, either \langle112\rangle and \langle100\rangle or \langle110\rangle and \langle111\rangle, which were consistent with a cyclic penta-
twinned crystal with five \{111\} twin boundaries arranged radially to the [110] direction of elongation. The nanorods have an idealized 3-D prismatic morphology with ten \{111\} end faces and five \{100\} or \{110\} side faces, or both. TEM studies of crystals at various stages of growth indicated that the seed crystals are initially transformed by growth and aggregation into decahedral penta-twinned crystals as shown in Figure 1.7.

**Figure 1.6.** (A) TEM image and the corresponding electron diffraction patterns recorded from individual Au nanorods, showing that orientations are close to [011]. (B) Dark-field TEM image recorded using a \{111\} reflected beam when a rod is oriented nearly parallel to the [110] direction and a structural model of the Au nanorods. (C) High-resolution TEM image recorded from an Au nanorod oriented along the [110] direction, displaying the \{100\}, \{111\} and \{110\} faceted crystal structure of the rod. Inset is the electron diffraction pattern recorded from the rod. *(Adapted from reference 25a)*
1.4. Growth Mechanism of Gold Nanorods

Mechanistic aspects related to the growth of Au nanorods have been investigated by various groups.\textsuperscript{27-32} A surfactant-directed metal nanorod growth mechanism was proposed by Murphy and coworkers which involves the differential blocking of certain crystallographic facets of Au nanorod (\{100\} or \{110\}) by CTAB which promotes the anisotropic growth of \{111\} edges.\textsuperscript{19} An alternate mechanism involving the electric field directed growth of Au nanorods was proposed by Perez-Juste et al. which suggests that the Au\textsuperscript{III} ions were initially bound to CTAB which upon reduction to Au\textsuperscript{I} ions interact more strongly with CTAB micelle. According to this mechanism the slow collision frequency of Au\textsuperscript{I} bound CTAB and the enhanced electric field at the tips allows the reduction of Au\textsuperscript{I} at the termini.\textsuperscript{29,30}
1.4.1. Surfactant Directed Mechanism

Surfactant-directed mechanism suggests that the CTAB head-group binds to the side surface of the Au nanorod through a preferential binding process. The Au atom spacing on the side faces is more comparable to the size of the CTAB head-group than the close-packed \{111\} face of gold, which is at the ends of the nanorods. Such binding stabilizes the side faces, which have relatively large surface energy and stress (tension) compared to other faces. This allows growth along the [110] common axis on \{111\} faces, which do not contain the CTAB headgroups. As judged by FTIR and thermogravimetric analysis, the hydrophobic tails of CTAB interdigitate to make a bilayer on the rods,\(^{31}\) with the cationic headgroups of the first monolayer facing the gold surface and the second layer facing the aqueous solvent (Figure 1.8).

![Figure 1.8. Cartoon illustrating the formation of the bilayer of CTAB on the nanorod (black rectangle) surface may assist nanorod formation as more gold ion (black dots) is introduced. (Adapted from reference 31)](image-url)
This mechanism is relevant only to (i) fcc metals whose growth starts with the single crystalline seed particles and (ii) the surface binding groups (surfactant/metal ions) that may preferentially bind to certain crystal faces of the seed or growing nanorods. CTAB in water forms rod-like micelles and directs the growth along short axis faces, by blocking the long axis crystal faces, resulting in nanorod formation.

1.4.2. Electric-Field Directed Growth Mechanism

The mechanism of electric field directed growth of nanorods proposes that the flux of Au\(^{I}\) bound to cationic micelles to the seed surface is maximum at points of large curvature, where the electrical double layer gradient is highest.\(^{30,32}\) The authors examined the nucleation and growth conditions more closely and pointed various parameters that induce the growth of rods. Binding of the Au\(^{III}\) and Au\(^{I}\) ions to the cationic micelles present in solution is the key phenomenon (Figure 1.9). The reduction of gold ions occurs when the micelles approach the seed particle, which is strongly influenced by the local electrical double layer interactions.

The rate of rod formation is determined by the frequency of collision of AuCl\(_2^-\) loaded cationic micelles with the cationic gold seed particles. This in turn is controlled by the electrical double layer interaction between the micelles and gold seed particles. Reduction of AuCl\(_4^-\) ions (Au\(^{III}\)) to AuCl\(_2^-\) ions (Au\(^{I}\)) by
ascorbate ions occurs on the micelle surface and the resultant complex remains tightly bound (Figure 1.9). During the encounter of this complex with the CTAB coated Au seed particles, gold ions may get discharged and the rate of the reaction is controlled by the collisions. Since the rate of collision of the complex is faster at tips than the sides, this would provide a direct pathway to nanorod formation (Figure 1.10).

**Figure 1.9.** Suggested mechanism for gold nanorod formation. AuCl₄⁻ ions are bound to cationic CTAB micelles, displacing Br⁻ ions. Reduction of AuCl₄⁻ to AuCl₂⁻ by ascorbate takes place on the micelles surface. AuCl₂⁻ remains adsorbed to the micelle. The transport of the bound gold ions to the growing seed particles is controlled by the double layer interaction of the cationic micelles with the gold seed coated with micelles. This favors deposition at the tips of the seeds, leading to rod formation. (*Adapted from reference 30*)

**Figure 1.10.** Surface charge density (σ) as a function of angle 2θ, as θ goes from zero (the tip) to 1/4 (the side). σ has been scaled by the value at the sides, showing the tip enhancement. (*Adapted from reference 30*)
1.5. Shape Anisotropic Properties of Gold Nanorods

In the case of noble metals such as Au, Ag and Cu, as the size decrease below the electron mean free path (the distance the electron travels between scattering collisions with the lattice centers), an intense absorption was observed in the UV-visible region. This result from the coherent oscillation of the free electrons from one surface of the particle to the other, which couples with the electromagnetic radiation, resulting in a strong absorption termed as surface plasmon absorption.\textsuperscript{33}

Gans investigated the shape dependence of the surface plasmon absorption\textsuperscript{34} and the simulated absorption spectra for nanorods as a function of their aspect ratio\textsuperscript{35} are shown in Figure 1.11. The observed absorption spectrum (Figure 1.11A) is much broader than the simulated one, due to the inhomogeneous broadening, which was not taken into account in the simulated spectra. Nanorods possess two plasmon absorption bands: one is due to the coherent electronic oscillation along the short axis (the transverse absorption band), and the other in the longer wavelength, which is more intense and results from the coherent electronic oscillation along the long axis\textsuperscript{36} (the longitudinal band). The longitudinal band undergoes a bathochromic shift with increasing aspect ratio of the nanorod.

The stability of Au nanorods is a major concern under exposure to light or heat. The thermodynamic tendency of lowering surface energy makes the rod like
nanostructures potentially unstable relative to the spherical nanoparticles. Slow heating of long micelles encapsulated gold nanorods undergoes decomposition (leading to the precipitation of gold nanorods) at temperature lower than those required for short micelles. This result in a decrease in the average length of nanorods and a blue shift in the longitudinal absorption maximum. Laser photothermal reshaping of the rods were also reported by laser excitation. At moderate energies, the femtosecond irradiation melts the nanorods to near spherical particles of comparable volumes, while the nanosecond pulses fragment them to smaller near-spherical particles.

Ultrafast emission, an interesting property observed in Au nanorods, were investigated by the time resolved fluorescence spectroscopy. The emission decay was found to be ≤50 fs. There are two principle processes which may be responsible for the emission from gold nanocrystals (i) direct (intraband) excitation of the surface plasmon resonance and emission from collective electron
motion\textsuperscript{40} and (ii) excitation of an interband transition followed by electron d-hole recombination emission,\textsuperscript{41} which is enhanced by a strong local field in the vicinity of the longitudinal surface plasmon resonance. Relative enhancement of ultrafast emission in gold nanorods of different aspect ratios were systematically compared with spherical nanoparticles and found that the emission is not sensitive to the wavelength of excitation.

Two-photon induced photoluminescence (TPI-PL) spectroscopy is an interesting tool for mapping the spatial distribution of the electric field near the nanorods, since the two-photon process is more sensitive to the local field strength than the single-photon process. The results\textsuperscript{42} revealed the characteristic features of plasmon modes in Au nanorods, as seen from photoluminescence images and the electric field distributions around the nanorods were mapped. The two peaks observed in the TPI-PL spectrum (Figure 1.12A) of a single gold nanorod were assigned to the electron-hole recombination near the X and L symmetry points, respectively. A photoluminescence image (Figure 1.12B) for short nanorods reveals that a strong field enhancement occurs at their ends. The photoluminescence image for a longer rod shows characteristic features reflecting an eigen function of a specific plasmon mode and holds good agreement with calculated electromagnetic local density of states.\textsuperscript{42c}
Chapter 1 – Gold Nanorods: An Overview

1.6. Applications of Gold Nanorods

Gold colloids have been used for several years as contrast agents in electron microscopy due to its electron-dense nature. Recently, gold and silver nanoparticles are used in biological optical imaging and sensing applications. Their applications in drug delivery, cancer cell diagnostics, and therapeutics have been active fields of research. The excellent elastic light scattering properties of metal nanoparticles, and the shift of the plasmon band maxima with local dielectric constant are some of the unique properties of Au nanorods. The photothermal properties of unusually shaped metal nanoparticles are of interest to the biomedical community. Gold nanostructures possess large absorption cross section in the near-infrared region and the absorbed light were dumped into the

Figure 1.12. (A) Two-photon-induced photoluminescence spectrum of a single gold nanorod. The dotted line shows a baseline at substrate. (B) Topographic images of gold nanorods (a, b). Two-photon-induced PL images (c, d) for a & b, respectively. Image sizes are 600 x 600 nm (a, c) and 700 x 700 nm (b, d). (Adapted from reference 42c)
surrounding media as heat, offering novel possibilities in cancer therapies (photothermal therapy).\(^{47}\)

### 1.6.1. Sensing and Imaging

Campigla and coworkers have developed a method for the detection of trace quantities of mercury present in tap water using Au nanorods.\(^{48}\) This method provides a direct way to determine mercury present in tap water samples at the parts-per trillion level (Figure 1.13). The outstanding selectivity and sensitivity results from the well-known amalgamation process that occurs between mercury and gold.\(^{49}\) Since active sites of Au nanorods are mainly at the tips of the nanostructures, amalgamation occurs efficiently at the tips of the nanorods, resulting in a decrease in their aspect ratio. Preferential deposition at the tips of the nanorods is also favored by the presence of densely packed surfactant (CTAB) molecules on the lateral sides of the nanorods. Their shielding effect restricts the amalgamation of mercury on the lateral walls of the nanorods. As a result there is a decrease in the aspect ratio of Au nanorods, which leads to a hypsochromic shift in the surface plasmon absorption. The entire procedure occurs within 10 min and does not involve elaborate sample preparation. The detection limit of $6.6 \times 10^{-13}$ g/L shows the excellent potential of Au nanorods for monitoring ultra low level of mercury in water samples.
Figure 1.13. (A) Schematic diagram showing the amalgamation of Hg with Au nanorods. (B) TEM and EDX analysis of Au nanorods in the absence and the presence of Mercury. I - No Hg; II - $1.25 \times 10^{-5}$ M and III - $1.57 \times 10^{-4}$ M Hg$^{2+}$. (Adapted from reference 48)

An ultra-sensitive medical imaging technique was reported by wang et al, by shining laser through the skin to detect tiny gold nanorods injected into the bloodstream. The test conducted in mice using Au nanorods yielded images nearly 60 times brighter than conventional fluorescent dyes (including rhodamine, commonly used for a wide range of biological imaging to study the inner functions of cells and molecules). Thus Au nanorods are promising candidate as an advanced medical imaging tool for the early detection of cancer and provide a possible way to overcome barriers in developing advanced medical imaging techniques, that use light to analyze blood vessels and underlying tissues.
1.6.2. Nanoconvertors

A near-infrared irradiation based photon-to-thermal energy conversion using nanosystems have been reported recently.\textsuperscript{51} Strong optical absorption behavior of noble metal nanoparticles is capable of creating a photothermal effect, i.e., an increase in temperature around the particle when it is illuminated by laser light.\textsuperscript{52} Extremely large photoabsorption cross sections and tunability in the surface plasmon resonance by varying the aspect ratios, make Au nanorods a highly efficient optothermal converter.\textsuperscript{53} Wang and coworkers imaged optothermal effect of Au nanorods by illuminating it individually with laser light (for 5 s), from below (at a distance of ca. 2 mm) and thermal images were recorded by an IR camera placed above each sample. Longer nanorods (aspect ratio of 5.5) exhibited a higher temperature rise than shorter nanorods. These experiments demonstrated that the optothermal conversion in gold nanorods is highly efficient.

1.6.3. Nanoresistors & Diodes

Multicomponent rod-like structures containing segments of dissimilar nanomaterials (metals,\textsuperscript{54} inorganic semiconductors and conducting polymers) exhibit resistor or diode like behavior. Such segmented nanorods may have potential applications in integrated microelectrode devices\textsuperscript{55} and synthesized through stepwise deposition. For example, segmented metal-polymer nanorods
were synthesized by electrochemical deposition of gold into alumina templates, followed by electrochemical polymerization of pyrrole (Ppy). The optical image of Au-Ppy-Au nanorods on top of a microelectrode array is shown in the inset of Figure 1.14A. The Au portions of the nanostructure (contacts 1-2 and 3-4, Figure 1.14A) exhibit linear $I-V$ plots over a voltage range from -1 to +1 V demonstrating Ohmic behavior. These systems can function as electrical leads in miniaturized circuits.

Devices constructed from single Au-Ppy-Cd-Au rods exhibit 'diode' behavior at room temperature (Figure 1.14B). The typical $I-V$ response was asymmetric and non-ohmic. In the forward bias, there is a positive voltage on the Au block adjacent to the Ppy and negative potential on the Au block interfaced with the Cd block. As a result the holes move from the Ppy block to the Cd block.

![Figure 1.14](image-url)

**Figure 1.14.** (A) Current-voltage ($I-V$) measurement for the gold blocks (1-2, 3-4) within a single nanorod at room temperature. Inset shows the optical microscope image of a single Au-Ppy-Au rod on prefabricated microelectrodes. (B) $I-V$ characteristics for a single Au-Ppy-Cd-Au rod at room temperature. *(Adapted from reference 55)*
during the forward bias. In reverse bias, current does not flow until the bias overcomes the breakdown potential (-0.61 V). The turn-on voltage for these diode nanorods is approximately 0.15 V. The diode behavior is attributed to the presence of an Ohmic and Schottky-like junctions at Ppy/Au and Ppy/Cd interfaces of the segmented rod.

1.6.4. Nanomotors & Machines

Sen and coworkers have recently reported\textsuperscript{56} that the nanorods made of gold at one end and platinum at the other can propel themselves around in a solution of dilute hydrogen peroxide, driven by the decomposition of H\textsubscript{2}O\textsubscript{2} catalyzed by platinum. Surprisingly, the rods move in the direction of the platinum end, suggesting that the oxygen produced by the reaction moves the rod by reducing the interfacial tension (rather than acting as a rocket exhaust). These motion, though non-Brownian, still went off in random directions, much like a bacterium’s motion in the absence of stimuli. The speed of two to ten body lengths per second was comparable to bacterial swimming.

Later the researchers have reined in their nanoscopic speedboats with a guidance system resembling that of magnetotactic bacteria. Two small (100 nm wide) segments of ferromagnetic nickel, incorporated between the segments of precious metals (Au & Pt), allow the rod to respond to guidance by magnetic fields\textsuperscript{57} (Figure 1.15). Using detailed statistical analysis, they showed that the field
provides only orientation, while the driving force continues to arise from the
catalyzed decomposition of H$_2$O$_2$. Tethering the rods to other components might
‘result in new classes of nano/micromachines’.

**Figure 1.15.** (A) SEM image of 1.5 μm X 400 nm striped metallic rod. Respective segment sizes (nm): Au, 350; Ni, 100; Au, 200; Ni, 100; Pt, 550. (B) The trajectory path of a Pt/Ni/Au/Ni/Au nanorod spelling the letters “PSU” in 5 wt % H$_2$O$_2$. (Adapted from reference 56)

### 1.7. Objectives of the Present Work

Gold nanorods have emerged as an attractive building block for nanoscale
devices; however integrating them into higher order assembly remains a major
challenge. The objectives of the present work are to (i) develop a new
methodology for the synthesis of monodispersed Au nanorods; (ii) tuning the
optical properties of Au nanorods by organizing them by adopting supramolecular
and covalent approaches and (iii) design sensors based on Au nanorods for the
selective detection of biologically important molecules.
1.8. References


Chapter 1 - Gold Nanorods: An Overview


Chapter I – Gold Nanorods: An Overview


