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Synthesis and Application of Nanorods

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1. Introduction

In nanotechnology, nanorods are morphology of nanoscale objects. Each of their dimension ranges from 1–100 nm. Nanorods may be synthesized from metals or semiconducting materials with ratios (length divided by width) are 3-5. One way for synthesis of nanorods is produced by direct chemical synthesis. The combinations of ligands act as shape control agents and bond to different facets of the nanorod with different strengths. This allows different faces of the nanorod to grow at different rates, producing an elongated object.

Gold nanorods are considered excellent candidates for biological sensing applications because the absorbance band changes with the refractive index of local material [1], allowing for extremely accurate sensing. In addition, nanorods with near-infrared absorption peaks can be excited by a laser at the absorbance band wavelength to produce heat, potentially allowing for the selective thermal destruction of cancerous tissues [2].

Nanoscale materials such as fullerenes, quantum dots and metallic nanoparticles have unique properties, because of their high surface area to volume ratio [3]. Gold nanospheres and nanorods also have unique optical properties, because of the quantum size effect [4]. Gold nanorods are cylindrical rods which range from less than ten to over forty nanometers in width and up to several hundred nanometers in length. These particles are typically characterized by their aspect ratio (length divided by width) [5-6].

In order to study and exploit the unique properties of nanorods, it is necessary to have a robust extinction coefficient which can predict the concentration of a solution at a particular absorbance. It is difficult to accurately obtain a measure of nanoparticle (as opposed to metal atom) concentration in moles per liter[2]. No spectroscopic device can provide concentration data, and only approximations are currently available.

Biomedical applications of nanoparticles require nanorods to be capped with biological molecules such as antibodies.

The El-Sayed method of nanorod concentration determination [7-8] is currently the standard way of measuring extinction coefficients ($\varepsilon$), and involves the coupling of bulk gold concentration, Transmission Electron Microscopy (TEM) size analysis and absorbance data. Recently, Liao and Hafner calculated $\varepsilon$ values of nanorods by preparing films of immobilized nanorods [2]. Liao and Hafner note that spherical byproducts lower the
extinction coefficient calculated by the El-Sayed method, but they do not discuss the sensitivity of ε to this kind of error.

Synthesis of gold nanorods has recently undergone dramatic improvements. It is possible to produce high yields of nearly monodispersed short gold nanorods [6-7,9]. The rods synthesized for this chapter were synthesized using Murphy’s method [9]. First, a “seed” solution of spherical gold nanoparticles was prepared by adding the following:

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Quantity(ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M HAuCl₄.3H₂O</td>
<td>0.250</td>
</tr>
<tr>
<td>0.1 M CTAB (cetyltrimethylammonium bromide)</td>
<td>7.5</td>
</tr>
<tr>
<td>0.01 M NaBH₄</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table. 1. Preparation of Gold seed

NaBH₄ reduces the gold salt to form nanoparticles, and cetyltrimethylammonium bromide (CTAB) (Fig.1) is a surfactant which stabilizes the seeds to prevent aggregation. To make nanorods, the reagents in Table.1 are added in order from top to bottom. Gold rods are synthesized with a small amount of silver to control rod size and make short rods [7,9]. CTAB is a directing surfactant; without it, only spheres would form. CTAB forms a rod shaped template that is filled with gold atoms as they are reduced by ascorbic acid. Ascorbic acid is a weaker reducing agent than NaBH₄, but in the presence of seeds and a CTAB template, it reduces gold ions at the seed surface [6].

2. Synthesis of nanorods

General idea is the same as the growth of nanorods (seed-mediated method)

To make surfactant-coated nanorods, the well-documented seed-mediated procedure developed by was employed. This method yields nanorods that are stabilized as verified from transmission electron microscopy (TEM) analysis [10].

Slightly change the conditions when growing nanorods (concentration of different reactants)

The nanorods were coated with a very thin (ca. 3-5 nm) silica film that

i. improved the colloidal stability of the nanorods by reducing aggregation,
ii. improved the shape stability of the nanorods, and
iii. allowed for further modification of the nanorod surface.

This silication method was first developed for citrate-stabilized (Fig.2.) gold NPs,[11-13] and has been applied successfully to gold nanorods[14-19].

Cubes, hexagon, triangle, tetropods, branched

A two-step growth method has been developed to grow nanorods by changing the oxygen content in gas mixture during nucleation and growth steps. This is based on our systematic studies of nucleation and growth under different conditions. Due to the large lattice mismatch (~;18%) between molecule and sapphire, the nucleation of molecule on sapphire
follows the three-dimensional island growth; that is, the Volmer–Weber mode, as reported by Yamauchi et al. in their observation of plasma-assisted epitaxial growth of molecule on sapphire [20,21]. At high temperature, the nucleation of nanorods islands on the surface of substrates depends strongly on the amount of active oxygen. When grown entirely in 90% oxygen plasma, nanorods has a high nucleation density and forms.

Direct chemical synthesis and a combination of ligands are all that are required for production and shape control of the nanorods. Ligands also bond to different facets of the nanorod with varying strengths. This is how different faces of nanorods can be made to grow at different rates, thereby producing an elongated object of a certain desired shape.

![Fig. 1. Growth mechanism of nanorods](image)

We synthesized silver nanorods with the average length of 280 nm and diameters of around 25 nm were synthesized by a simple reduction process of silver nitrate in the presence of polyvinyl alcohol (PVA) and investigated by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission-electron microscopy (TEM).

It was found out that both temperature and reaction time are important factors in determining the morphology and aspect ratios of nanorods (Fig.2.). TEM images showed the prepared silver nanorods have a face centered shape (fcc) with fivefold symmetry consisting of multiply twinned face centered cubes as revealed in the cross-section observations. The five fold axis, i.e. the growth direction, normally goes along the (111) zone axis direction of the basic fcc Ag-structure. Preferred crystallographic orientation along the (111), (200) or (220) crystallographic planes and the crystallite size of the silver nanorods are briefly analyzed [22-26].
In our research, synthesis of silver nanorods with the controllable dimensions was described by using a reducing agent that involves the reduction of silver nitrate with N-N’-Dimethyl formamide (DMF) in the presence of PVA as a capping reagent. In this process the DMF is served as both reductant and solvent [27, 28]. SEM and TEM observations (fig. 2, 3) along a series of relevant directions show that the silver nanorods have an average length of 280 nm and diameters of around 25 nm. TEM observations from cross section of nanorods show that the transformation of silver nanospheres to silver nanorods is achieved by the oriented attachment of several spherical particles followed by their fusion. Resulted Ag-nanorods have a twinned fcc structure, appeared in a pentagonal shape with fivefold twinning. The fivefold axis, i.e. the growth direction, normally goes along the (110) zone axis direction of the fcc cubic structure. The XRD data (fig. 4) confirmed that the silver nanorod is crystalline with fcc structure with a preferred crystallographic orientation along the (220) direction and straight, continuous, dense silver nanorod has been obtained with a diameter 25 nm. [22].

On the other hand, gold nanorods were prepared by adopting a photochemical method that employs UV-irradiation to facilitate slow growth of rods Tetraoctylammonium bromide as a co-surfactant used instead of tetradodecylammonium bromide. The growth solution was prepared by dissolving 440 mg of cetyltrimethylammonium bromide (CTAB) and 4.5 mg of
tetraoctylammonium bromide (TOAB) in 15 mL of water and transferred to a cylindrical quartz tube (length 15 cm and diameter 2 cm). To this solution, 1.25 mL of 0.024 M HAuCl₄ solution was added along with 325 µL of acetone and 225 µL of cyclohexane. The formation of the gold nanorod and its aspect ratio was confirmed from Transmission Electron Microscopic analysis. A drop of a dilute solution of Au nanorods was allowed to dry on a carbon coated copper grid and then probed using a JEOL JEM-100sx electron microscope. The average length and diameter of rods employed in the present investigation are 50.0 nm and 20.0 nm, respectively and an average aspect ratio of 2.5 [29].

Fig. 4. XRD pattern of Ag/PVA nanocomposite indicative the face-centered cube structure.

Changes in nanorod dimensions have the greatest impact on extinction coefficients. Fig.5(a) shows the change in the Beer’s law plot with increasing polydispersity. As variation in the rod dimensions increases, the extinction coefficient increases. However, these increases are not excessive – from 3.85 ± 0.07 to 4.90 ± 0.08 x 10⁻⁸ M is not significant, and errors in concentration resulting from this magnitude of change in ε would not be enough to cause aggregation or substantial miscalculations of antibodies. However, the effect of spherical
byproducts is more pronounced, and the presence of spheres can alter the extinction coefficient enough to cause concern.

Fig. 5(b) shows that the extinction coefficient nearly doubles as percentage of spherical byproducts is increased from 5% to 40%. Spherical byproducts are an ongoing challenge in nanorods synthesis, and it is important to consider how they can change the extinction coefficient.

![Graph showing the effect of error on extinction coefficient](image)

The ranges of extinction coefficients found in this model are quite different from the values calculated by [2] and [6], which were on the order of 10^9 M. However, the rods used in these calculations, while of approximately the same aspect ratio, had dimensions of 50 x 15 nm instead of 30 x 8 nm. The same aspect ratio implies the same peak wavelength, but can result in a different rod volume (and thus different concentration measurements). Small changes

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in aspect ratio can substantially change absorbance peak location [7]. Literature values must be used cautiously in nanorod studies.

4. Application of nanorod

Nanorods have wide application.

4.1 Nanorods for dye solar cells

The dye-solar cell (DSC or Grätzel) first presented in 1991 offers an interesting paradigm with regards the generation of electricity directly from sunlight via the photovoltaic effect. In essence the DSC is not a definite structure but more a design philosophy to mimicking nature in the conversion of solar energy [30]. The DCS is formed by an electrode, preferably with a large internal surface area onto which is attached a light absorbing dye. The dye upon absorption of a photon by photo-excitation of an electron (moving from the HOMO to the LUMO levels) will, if in favourable conditions, inject the photo-excited electron into the supporting structure. The dye is regenerated by a supporting Reduction & Oxidation (REDOX) electrolyte (or hole conducting semiconductor) which permeates the working electrode [31]. One of the many components of the DSC that can be altered is the working electrode. General requirements are that it be porous (i.e. large internal surface area) and be n-type semiconducting. Several metal-oxides fulfil these requirements (e.g., TiO₂, ZnO, WO₃) [32].

There are several reports describing the electrodeposition of ZnO with various conditions explored resulting in a variety of geometries as for e.g., nanorods, nanoneedles, nanotubes, nanoporous and compact layers [33]. In this work, a high-density vertically aligned ZnO nanorods arrays, Fig. 6, were prepared on fluorine doped SnO₂ (FTO) coated glass substrates, prepared at 70 °C from a neutral zinc nitrate solution, varying the deposition time.

![Fig. 6. Cross section view of ZnO nanorod arrays electrodeposited on FTO glass](image-url)
4.2 The use of nanorods for oligonucleotide detection

Functionalization of nanoparticles with biomolecules (antibodies, nucleic acids, etc.) is of interest for many biomedical applications [34]. One of the most perspectives is application of gold nanorods (GNRs) for detecting target sequences of infecting agents of many dangerous diseases, for example, a HIV-1 [35]. The method is based on electrostatic interaction between GNRs and DNA molecules. As single-stranded DNA molecules are zwitterions, and double-stranded are polyanions, their affinity towards polycationic GNR stabilizer (cetiltrimetilammoniumbromide, CTAB) is various. The GNRs plasmon-resonant [7-8] labels are functionalized with probe single-stranded oligonucleotides by physical adsorption or by chemical attachment. By adding complement targets to the GNRs-probe conjugate solution a formation of aggregates is observed. It has been shown recently [35] that GNRs aggregation, induced by DNA-DNA hybridization on their surface, can be detected by extinction and scattering spectroscopy techniques. We have found that the characteristic parameter of biospecific interaction is change of amplitude and differential light scattering method for detection DNA-DNA interaction. This work is aimed at study of aggregation properties of single-stranded probe DNA-GNRs conjugates as applied to biospecific detection of target oligonucleotides (fig.7).

![Experimental diagram for oligonucleotide detection](https://www.intechopen.com)

1. Initial nanorod sample (NRs-750)  
2. NRs-750 + H₂O + Tris-HCl + probe + NaCl  
3. NRs-750 + H₂O + Tris-HCl + probe + NaCl + target  

Fig. 7. Experimental diagram for oligonucleotide detection
In Fig. 8, first the nanorods were coated with a thin silica layer using the silane coupling agent, MPTMS, followed by reaction with sodium silicate. Surface-bound aldehyde functional groups were attached to the silica film by using TMSA and then used to conjugate the amine-modified DNA in a reductive amination reaction.

GNRs were produced by seed-mediated growth method in presence of CTAB. Extinction and scattering spectra were measured in the wavelength range from 450 to 900 nanometers which includes the transversal and longitudinal plasmon resonance [7-8] bands of GNRs. The particle and aggregate average size were measured by the dynamic light scattering method (DLS), and the particle shape and cluster structure were examined by transmission electron microscopy (TEM). 21-mer oligonucleotide complement pair was taken as a biospecific pair, and the target sequence was related to human immunodeficiency virus-1 (HIV-1) genome. In this experiments demonstrated that reproducibility of aggregation test depends on the GNRs synthesis protocol. In particularly, the use of protocol [36] led to unsatisfactory results. According to TEM data, the method realization was successful while using «dog-bone» morphology particles.

The functionalized gold nanorod synthesis can be divided into three main steps:

- Gold Nanorod Fabrication.
- Silica Shell Formation.
- DNA Functionalization.
4.3 The use of nanorods for applied electric field

Prominent among them is in the use in display technologies. By changing the orientation of the nanorods with respect to an applied electric field, the reflectivity of the rods can be altered, resulting in superior displays. Picture quality can be improved radically. Each picture element, known as pixel, is composed of a sharp-tipped device of the scale of a few nanometers. Such TVs, known as field emission TVs, are brighter as the pixels can glow better in every color they take up as they pass though a small potential gap at high currents, emitting electrons at the same time.

Nanorod-based flexible, thin-film computers can revolutionize the retail industry, enabling customers to checkout easily without the hassles of having to pay cash.

The semiconductor nanorod structure is based on a junction between nanorod structure and another window semiconductor layer for solar cell application. The possibility of band gap tuning by varying the diameter of the nanorods along the length, higher absorption coefficient at nanodimensions, the presence of a strong electrical field at the nanorod-window semiconductor nanojunctions and the carrier confinement in lateral direction are expected to result in enhanced absorption and collection efficiency in the proposed device. Process steps, feasibility, technological tasks needed for the realization of the proposed structure and the novelty of the present structure in comparison to the already reported nanostructured solar cells are also discussed [37].

4.4 The use of nanorods for applied humidity sensitive

ZnO nanorod and nanowire films were fabricated on the Si substrates with comb type Pt electrodes by the vapor-phase transport method, and their humidity sensitive characteristics have been investigated. These nanomaterial films show high-humidity sensitivity, good long-term stability and fast response time. It was found that the resistance of the films decreases with increasing relative humidity (RH). At room temperature (RT), resistance changes of more than four and two orders of magnitude were observed when ZnO nanowire and nanorod devices were exposed, respectively, to a moisture pulse of 97% relative humidity. It appears that the ZnO nanomaterial films can be used as efficient humidity sensors [38]. The gas sensor fabricated from ZnO nanorod arrays showed a high sensitivity to H₂ from room temperature to a maximum sensitivity at 250 °C and a detection limit of 20 ppm. In addition, the ZnO gas sensor also exhibited excellent responses to NH₃ and CO exposure. Our results demonstrate that the hydrothermally grown vertically aligned ZnO nanorod arrays are very promising for the fabrication of cost effective and high performance gas sensors [39].

To use nanorods in biomedical applications, it is advised that samples are produced in bulk and ε is calculated for each batch. In addition, Nanorod aggregation, induced by biospecific interaction, was shown by four methods (extinction and scattering spectroscopy, DLS, TEM).

5. Conclusion

The mechanism of the nanorod formation is not yet completely understood. However, it has now been demonstrated that the necessary requirements are at least (i) a mild reducing agent, (ii) a protecting agent (for example consisting of a solution of PVA in DMF), and (iii)
the presence of metal ions in solutions. It is found that both temperature and reaction time are important factors in determining the morphology and aspect ratios of nanorods. Lower temperature and longer time are favorable to form polycrystalline metal nanorods with high uniformity and aspect ratios. In addition to the nanoparticles with controllable size, silver nanorods were successfully synthesized by converting nanoparticles at a relatively low temperature of 80°C. We believe that the detailed investigation of silver nanorods [22] will also help us to synthesize other metal nanorod more easily by using the similar technique.

6. Acknowledgment

The financial and encouragement support provided by the Research vice Presidency of Tonekabon Branch, Islamic Azad University and Executive Director of Iran-Nanotechnology Organization (Govt. of Iran).

7. References

Nanorods

[31] Q. Zhang, G. Cao, Nano Today 6 (2011) 91;
The book “Nanorods” is an overview of the fundamentals and applications of nanosciences and nanotechnologies. The methods described in this book are very powerful and have practical applications in the subjects of nanorods. The potential applications of nanorods are very attractive for bio-sensor, magneto-electronic, plasmonic state, nano-transistor, data storage media, etc. This book is of interest to both fundamental research such as the one conducted in Physics, Chemistry, Biology, Material Science, Medicine etc., and also to practicing scientists, students, researchers in applied material sciences and engineers.

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