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Preparation and Characterization of Gold Nanorods

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1. Introduction

Numerous characteristics of nanomaterials depend on size and shape, including their catalytic, optical, electronic, chemical and physical properties. The shape and crystallographic facets are the major factors in determining the catalytic and surface activity of nanoparticles. The size can influence the optical properties of metal nanoparticles. This is especially important when the particles have aspect ratios (length/diameter, L/D) larger than 1. So, in the synthesis of metal nanoparticles, control over the shape and size has been one of the important and challenging tasks.

A number of chemical approaches have been actively explored to process metal into one-dimensional (1 D) nanostructures. Among these objects of study, rodlike gold nanoparticles are especially attractive, due to their unique optical properties and potential applications in future nanoelectronics and functional nanodevices. Gold nanorods show different color depending on the aspect ratio, which is due to the two intense surface plasmon resonance peaks (longitudinal surface plasmon peak and transverse surface plasmon peak corresponding to the oscillation of the free electrons along and perpendicular to the long axis of the rods) (Kelly et al., 2003). The color change provides the opportunity to use gold Nanorods as novel optical applications. Gold nanorods are used in molecular biosensor for the diagnosis of diseases such as cancer, due to this intense color and its tunability. Nanorods also show enhanced fluorescence over bulk metal and nanospheres, which will prove to be beneficial in sensory applications. The increase in the intensity of the surface plasmon resonance absorption results in an enhancement of the electric field and surface enhanced Raman scattering of molecules adsorbed on gold nanorods. All these properties make gold nanorod a good candidate for future nanoelectronics (Park, 2006). In this chapter, we will describe the preparation and characterization of gold nanorods.

2. Preparation of gold nanorods

Although quite a few approaches have been developed for the creation of gold nanorods, wet chemistry promises to become the preferred choice, because of its relative simplicity and use of inexpensive materials. There are three main methods used to produce gold rods through wet chemistry. Chronological order is followed, which in turn implies successive improvement in material quality. Each new method is also accompanied by a decrease in difficulty of the preparation (Pérez-Juste et al., 2005).

2.1 Template method

The template method for the preparation of gold nanorods was first introduced by Martin and co-workers (Foss, 1992; Martin, 1994, 1996). The method is based on the electrochemical deposition of Au within the pores of nanoporous polycarbonate or alumina template membranes. The rods could be dispersed into organic solvents through the dissolution of the appropriate membrane followed by polymer stabilization (Cepak & Martin, 1998). The method can be explained as follows: initially a small amount of Ag or Cu is sputtered onto the alumina template membrane to provide a conductive film for electrodeposition. This is used as a foundation onto which the Au nanoparticles can be electrochemically grown (stage I in Fig. 1). Subsequently, Au is electrodeposited within the nanopores of alumina (stage II). The next stage involves the selective dissolution of both the alumina membrane and the copper or silver film, in the presence of a polymeric stabilizer such as poly(vinyl pyrrolidone) (III and IV in the Fig. 1). In the last stage, the rods are dispersed either in water or in organic solvents by means of sonication or agitation (Pérez-Juste et al., 2005).

The length of the nanorods can be controlled through the amount of gold deposited within the pores of the membrane (van der Zande et al., 2000). The diameter of the gold nanoparticles thus synthesized coincides with the pore diameter of the alumina membrane. So, Au nanorods with different diameters can be prepared by controlling the pore diameter of the template (Hulteen & Martin, 1997; Jirage et al., 1997). The fundamental limitation of the template method is the yield. Since only monolayers of rods are prepared, even milligram amounts of rods are arduous to prepare. Nevertheless, many basic optical effects could be confirmed through these initial pioneering studies.

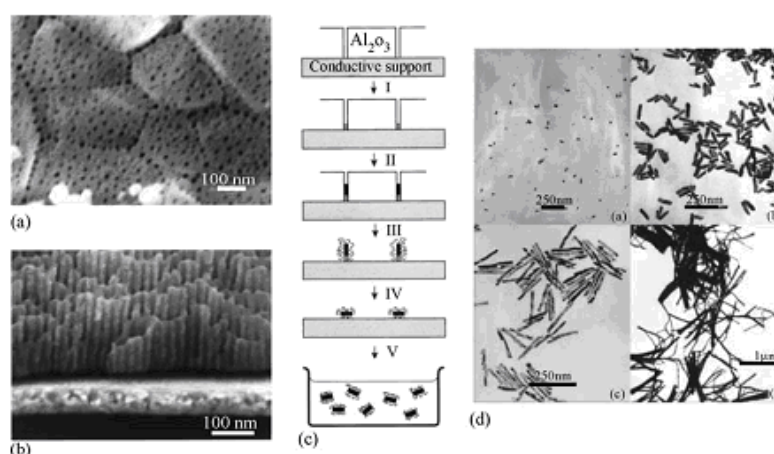


Fig. 1. (a and b) Field emission gun-scanning electron microscopes images of an alumina membrane. (c) Schematic representation of the successive stages during formation of gold nanorods via the template method. (d) TEM micrographs of gold nanorods obtained by the template method (van der Zande et al., 2000).

2.2 Electrochemical method

An electrochemical route to gold nanorod formation was first demonstrated by Wang and co-workers (Chang et al., 1997, 1999). The method provides a synthetic route for preparing high yields of Au nanorods. The synthesis is conducted within a simple two-electrode type electrochemical cell, as shown in the schematic diagram in Fig. 2A.

In the representative electrochemical process, the following conditions are necessary and important:

1. A gold metal plate (3 cm×1 cm×0.05 cm) as a sacrificial anode
2. A platinum plate similar as a cathode (3 cm×1 cm×0.05 cm)
3. A typical current of 3 mA and a typical electrolysis time of 30 min
4. Electrolytic solutions to immerse the both electrodes at 36 °C, it contained:

A cationic surfactant, for example: hexadecyltrimethylammonium bromide ($C_{16}TAB$) to support the electrolyte and to behave as the stabilizer for the nanoparticles to prevent aggregation.

A small amount of a tetradodecylammonium bromide ($TC_{12}AB$), which acts as a rod-inducing cosurfactant.

Appropriate amount of acetone added to the electrolytic solution for loosening the micellar framework to assist the incorporation of the cylindrical-shape-inducing cosurfactant into the $C_{16}TAB$ micelles.

Suitable amount of cyclohexane to enhance the formation of elongated rod-like $C_{16}TAB$ micelles.

A silver plate is gradually immersed close to the Pt electrode to control the aspect ratio of Au nanorods.

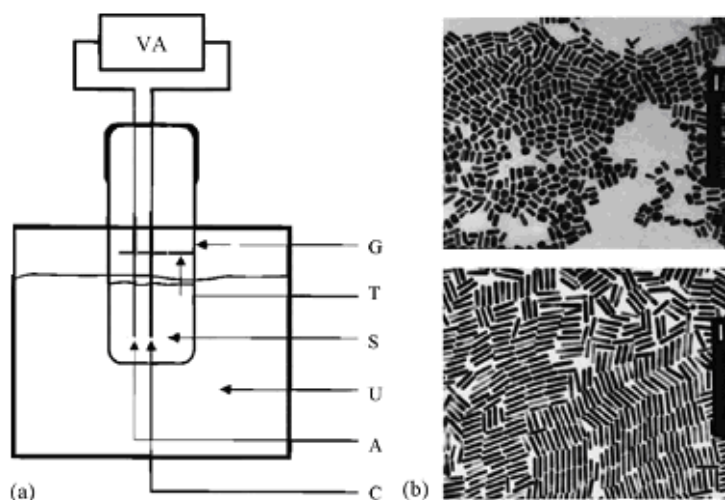


Fig. 2. (a) Schematic diagram of the set-up for preparation of gold nanorods via the electrochemical method containing; VA, power supply; G, glassware electrochemical cell; T, teflon spacer; S, electrode holder; U, ultrasonic cleaner; A, anode; C, cathode. (b) TEM micrographs of Au nanorods with different aspect ratios 2.7 (top) and 6.1 (bottom). Scale bars represent 50 nm (Chang, 1999).

During the synthesis, the bulk gold metal anode is initially consumed, forming $AuBr_4^-$. These anions are complexed to the cationic surfactants and migrate to the cathode where reduction occurs. It is unclear at present whether nucleation occurs on the cathode surface or within the micelles. Sonication is needed to shear the resultant rods as they form away from the surface or possibly to break the rod off the cathode surface. Another important

factor controlling the aspect ratio of the Au nanorods is the presence of a silver plate inside the electrolytic solution, which is gradually immersed behind the Pt electrode. The redox reaction between gold ions generated from the anode and silver metal leads to the formation of silver ions (Pérez-Juste et al., 2005). Wang and co-workers found that the concentration of silver ions and their release rate determined the length of the nanorods. The complete mechanism, as well as the role of the silver ions, is still unknown.

2.3 Seeded growth method

Seeded growth of monodisperse colloid particles dates back to the 1920s. Recent studies have successfully led to control of the size distribution in the range 5-40 nm, whereas the sizes can be manipulated by varying the ratio of seed to metal salt (Jana et al., 2001). In the presence of seeds can make additional nucleation takes place. Nucleation can be avoided by controlling critical parameters such as the rate of addition of reducing agent to the metal seed, metal salt solution and the chemical reduction potential of the reducing agent. The step-by-step particle enlargement is more effective than a one step seeding method to avoid secondary nucleation. Gold nanorods have been conveniently fabricated using the seeding-growth method (Carrot et al., 1998).

The preparation of 3.5 nm seed solution can be explained as follows: C₁₆TAB solution (5.0 mL, 0.20 M) was mixed with 2.0 mL of 5.0×10⁻⁴ M HAuCl₄. To the stirred solution, 0.60mL of ice-cold 0.010 M NaBH₄ was added, which resulted in the formation of a brownish yellow solution. After vigorous stirring of the seed solution for 2 min, it was kept at 25 °C without further stirring. The seed solution was used between 2 and 48 h after its preparation (Jana et al., 2001).

By controlling the growth conditions in aqueous surfactant media it was possible to inhibit secondary nucleation and synthesize gold nanorods with tunable aspect ratio. Some reserches showed addition of AgNO₃ influences not only the yield and aspect ratio control of the gold nanorods but also the mechanism for gold nanorod formation, correspondingly its crystal structure and optical properties (Pérez-Juste et al., 2005). At this point, it is thus convenient to differentiate seed-mediated approaches performed in the absence or in the presence of silver nitrate.

2.3.1 Preparation of gold nanorods without AgNO₃

Murphy and co-workers were able to synthesize high aspect ratio cylindrical nanorods using 3.5 nm gold seed particles prepared by sodium borohydride reduction in the presence of citrate, through careful control of the growth conditions, i.e., through optimization of the concentration of C₁₆TAB and ascorbic acid, and by applying a two- or three- step seeding process (see Fig.3).

(1) Preparation of 4.6±1 Aspect Ratio Rod.

In a clean test tube, 10 mL of growth solution, containing 2.5×10⁻⁴ M HAuCl₄ and 0.1 M C₁₆TAB, was mixed with 0.05 mL of 0.1 M freshly prepared ascorbic acid solution. Next, 0.025 mL of the 3.5 nm seed solution was added without further stirring or agitation. Within 5-10 min, the solution color changed to reddish brown. The solution contained 4.6 aspect ratio rods, spheres, and some plates. The solution was stable for more than one month (Jana et al., 2001).

(2) Preparation of 13 ± 2 Aspect Ratio Rod.

A three-step seeding method was used for this nanorod preparation. Three test tubes (labeled A, B, and C), each containing 9 mL growth solution, consisting of 2.5×10^{-4} M HAuCl_4 and 0.1 M C_{16}TAB , were mixed with 0.05 mL of 0.1 M ascorbic acid. Next, 1.0 mL of the 3.5 nm seed solution was mixed with sample A. The color of A turned red within 2-3 min. After 4-5 h, 1.0 mL was drawn from solution A and added to solution B, followed by thorough mixing. The color of solution B turned red within 4-5 min. After 4-5 h, 1 mL of B was mixed with C. Solution C turned red in color within 10 min. Solution C contained gold nanorods with aspect ratio 13. All of the solutions were stable for more than a month (Jana et al., 2001).

(3) Preparation of 18 ± 2.5 Aspect Ratio Rod.

This procedure was similar to the method for preparing 13 aspect ratio rods. The only difference was the timing of seed addition in successive steps. For 13 aspect ratio rods, the seed or solutions A and B were added to the growth solution after the growth occurring in the previous reaction was complete. But to make 18 aspect ratio rods, particles from A and B were transferred to the growth solution while the particles in these solutions were still growing. Typically, solution A was transferred to B after 15 s of adding 3.5 nm seed to A, and solution B was transferred to C after 30 s of adding solution A to B (Jana et al., 2001).

In the above method, the yield of the nanorods thus synthesized is ca. 4 % (Jana et al., 2001). The long rods can be concentrated and separated from the spheres and excess surfactant by centrifugation. Later, the same group reported an improved methodology to produce monodisperse gold nanorods of high aspect ratio in 90 % yield (Busbee et al., 2003), just through pH control. In the new proposed protocol, addition of sodium hydroxide, equimolar in concentration to the ascorbic acid, to the growth solution raised the pH. The pH of the growth solution was changed from 2.8 to 3.5 and 5.6, which led to the formation of gold nanorods of aspect ratio 18.8 ± 1.3 and 25.1 ± 5.1 , respectively. The newer procedure also, resulted in a dramatic increase in the relative proportion of nanorods and reduced the separation steps necessary to remove smaller particles.

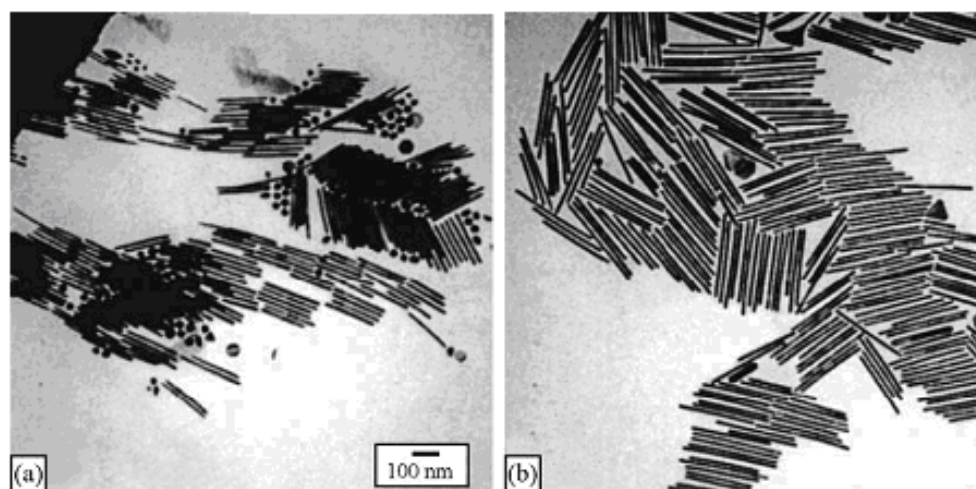


Fig. 3. TEM images of shape-separated 13 (a) and 18 (b) aspect ratio gold nanorods prepared by the seed-mediated method (Jana et al., 2001).

The mechanism of formation of rod-shaped nanoparticles in aqueous surfactant media remains unclear. Based on the idea that C₁₆TAB adsorbs onto gold nanorods in a bilayer fashion, with the trimethylammonium headgroups of the first monolayer facing the gold surface (Nikoobakht et al., 2001), Murphy and co-workers (Johnson et al., 2002) proposed that the C₁₆TAB headgroup preferentially binds to the crystallographic faces of gold existing along the sides of pentahedrally twinned rods, as compared to the faces at the tips. The growth of gold nanorods would thus be governed by preferential adsorption of C₁₆TAB to different crystal faces during the growth, rather than acting as a soft micellar template (Johnson et al., 2002). The influence of C_nTAB analogues in which the length of the hydrocarbon tails was varied, keeping the headgroup and the counterion constant was also studied (Gao et al., 2003). It was found that the length of the surfactant tail is critical for controlling not only the length of the nanorods but also the yield, with shorter chain lengths producing shorter nanorods and longer chain lengths leading to longer nanorods in higher yields (Pérez-Juste et al., 2005).

Considering the preferential adsorption of C₁₆TAB to the different crystal faces in a bilayer fashion (Nikoobakht et al., 2001; Johnson et al., 2002; Gao et al., 2003), a “zipping” mechanism was proposed taking into account the van der Waals interactions between surfactant tails within the surfactant bilayer, on the gold surface, that may promote the formation of longer nanorods from more stable bilayers (see Fig. 4) (Gao et al., 2003).

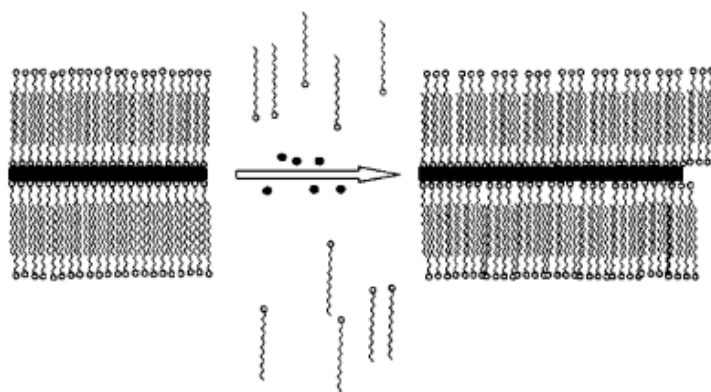


Fig. 4. Schematic representation of “zipping”: the formation of the bilayer of C_nTAB (squiggles) on the nanorod (black rectangle) surface may assist nanorod formation as more gold ions (black dots) are introduced (Gao et al., 2003).

Recently, Pérez-Juste et al. investigated the factors affecting the nucleation and growth of gold nanorods under similar conditions (Pérez-Juste et al., 2004). They showed that the aspect ratio, the monodispersity and the yield could be influenced by the stability of the seed, temperature, the nature and concentration of surfactant. The yield of nanorods prepared from C₁₆TAB capped seeds is much higher than that from naked (or citrate stabilized) seeds. This indicates that the more colloiddally stable the gold seed nanoparticles are, the higher the yield of rods.

2.3.2 Preparation of Gold Nanorods with AgNO₃

The presence of silver nitrate allows better control of the shape of gold nanorods synthesized by the electrochemical method, and Murphy and co-workers proposed a

variation of their initial procedure for long nanorods (Jana et al., 2001), in order to increase the yield of rod-shaped nanoparticles (up to 50 %) and to control the aspect ratio of shorter nanorods and spheroids (Jana et al., 2001). Under identical experimental conditions, a small amount of silver nitrate is added (5×10^{-6} M) prior to the growth step. The aspect ratio of the spheroids and nanorods can be controlled by varying the ratio of seed to metal salt, as indicated in the spectra of Fig.5. The presence of the seed particles is still crucial in the growth process, and there is an increase in aspect ratio when the concentration of seed particles is decreased.

The mechanism by which Ag^+ ions modify the metal nanoparticle shape is not really understood. It has been hypothesized that Ag^+ adsorbs at the particle surface in the form of AgBr (Br^- coming from C_{16}TAB) and restricts the growth of the AgBr passivated crystal facets (Jana et al., 2001). The possibility that the silver ions themselves are reduced under these experimental conditions (pH 2.8) can be neglected since the reducing power of ascorbate is too positive at low pH (Pal et al., 1998). This shape effect depends not only on the presence of AgNO_3 , but also on the nature of the seed solution. By simply adjusting the amount of silver ions in the growth solution, a fine-tuning of the aspect ratio of the nanorods can be achieved, so that an increase in silver concentration (keeping the amount of seed solution constant) leads to a redshift in the longitudinal plasmon band. Interestingly, the aspect ratio can also be controlled by adjusting the amount of seed solution added to the growth solution in the presence of constant Ag^+ concentration (Pérez-Juste et al., 2004). Contrary to expectations, an increase in the amount of seed produces a red-shift in the longitudinal plasmon band position, as shown in Fig. 6, pointing toward an increase in aspect ratio.

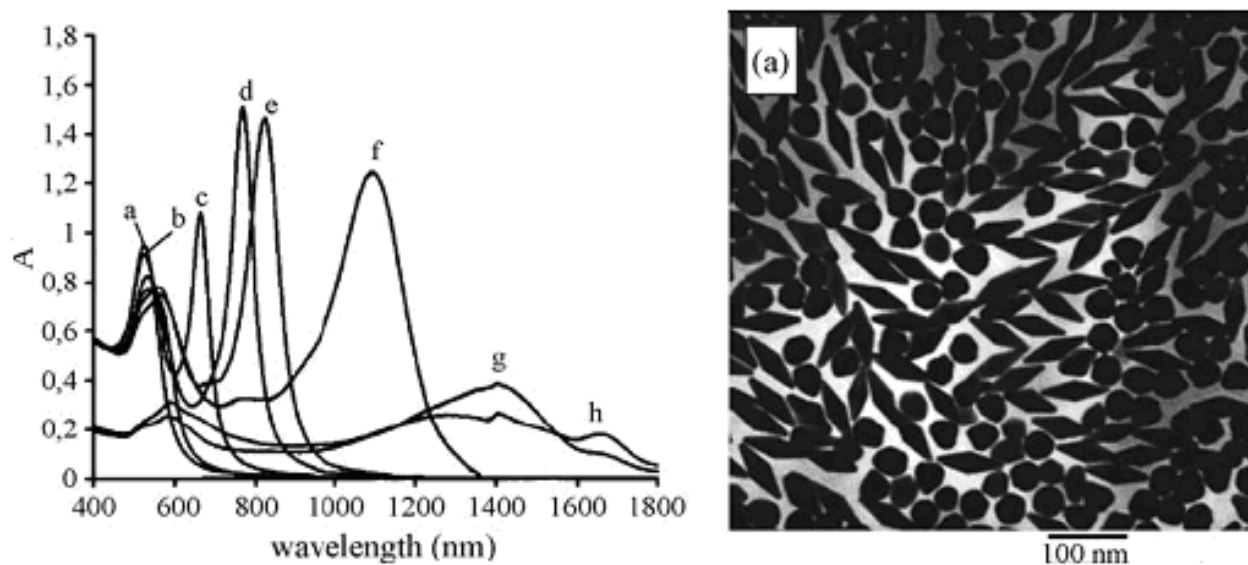


Fig. 5. UV-vis spectra of Au nanorods with increasing aspect ratios (a-h) formed by decreasing the amount of added seed (left). TEM image of Au nanorods synthesized in the presence of silver nitrate (right) (Jana et al., 2001; Jana et al., 2002).

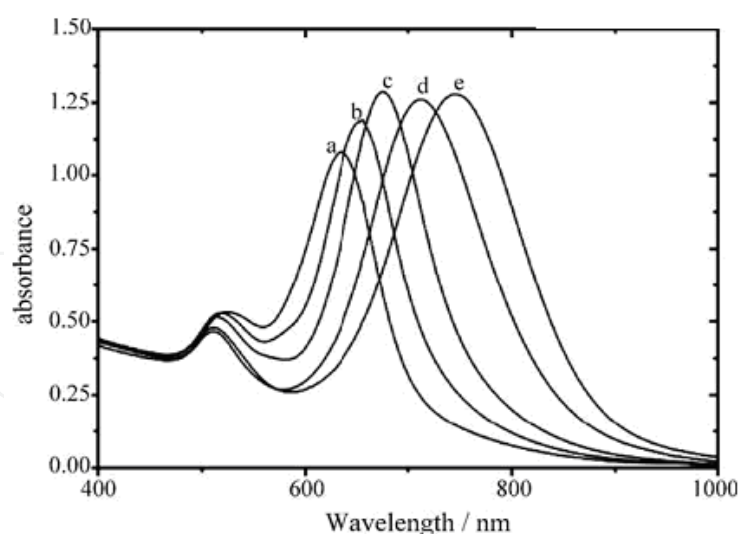


Fig. 6. UV-vis spectra of Au nanorods prepared in the presence of silver nitrate by the El-Sayed's protocol (Pérez-Juste et al., 2004).

2.4 Photochemical method

Yang and co-workers developed a photochemical method for the synthesis of gold nanorods (Kim et al., 2002), which is performed in a growth solution similar to that described for the electrochemical method (Chang et al., 1997), in the presence of different amounts of silver nitrate and with no chemical reducing agent.

The growth solution containing gold salts and others such as surfactants and reducing agents, was irradiated with a 254 nm UV light ($420 \mu\text{W}/\text{cm}^2$) for about 30 h. The resulting solution was centrifuged at 3000 rpm for 10 minutes, and the supernatant was collected, and then centrifuged again at 10,000 rpm for 10 minutes. The precipitate was collected and redispersed in deionized water. The colour of the resulting solution varies with the amount of silver ions added, which is indicative of gold nanorods with different aspect ratios (Boyes & Gai, 1997) as shown in Fig. 7.

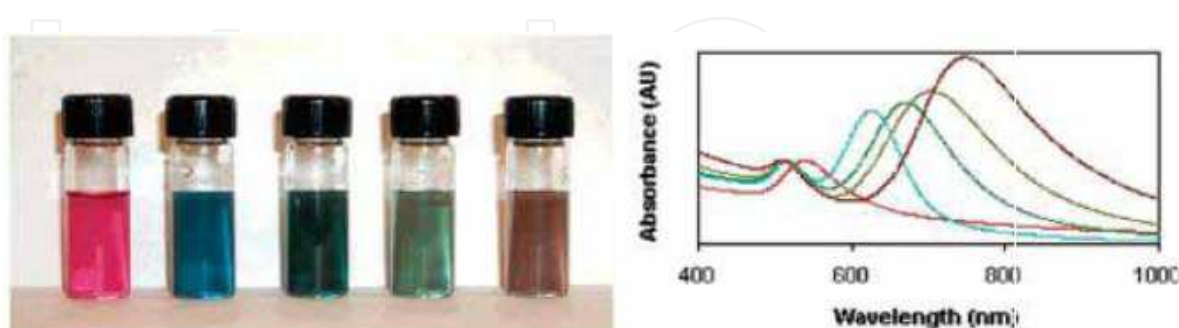


Fig. 7. (a) Image of photochemically prepared gold nanorods solution, and (b) corresponding UV-vis spectrum. The left most solution was prepared with no silver ion addition. The other solutions were prepared with addition of 15.8, 31.5, 23.7, 31.5 μL of silver nitrate solution, respectively. The middle solution was prepared with longer irradiation time (54 h) compared to that for all other solutions (30 h), and the transformation into shorter rods can be seen (Gai, 1998).

Seen from Fig. 7 two absorption peaks were obtained, which resulted from the longitudinal and transverse surface plasmon (in the UV-vis spectrum) that indicates gold nanorods are formed when silver ions are added (Gai, 1998). The aspect ratio increases when more silver ions are added, and this is accompanied by a decrease in rod width, while in the absence of silver ions, spherical particles are obtained. Therefore, the possibility of a rod-like micellar template mechanism can be discarded and these experiments indicate the critical role played by silver ions in determining the particle morphology.

2.5 Other methods

Markovich and co-workers adapted the seed-mediated method in the absence of silver nitrate proposed by Murphy and co-workers (Jana et al., 2001) for the growth of gold nanorods directly on mica surfaces (Taub et al., 2003). The method involves the attachment of the spherical seed nanoparticles to a mica surface, which is then dipped in a C₁₆TAB surfactant growth solution. About 15 % of the surface-bound seeds are found to grow as nanorods. This yield enhancement of nanorods, compared to that obtained for the solution growth technique (ca. 4 %) (Jana et al., 2001), was attributed to a change in the probability of the growing seed to develop twinning defects. Subsequently, Wei et al. adapted the method to grow nanorods directly on glass surfaces (Wei et al., 2004). They studied the influence of the linker used to attach the seed particles and the gold salt concentration in the growth solution on the formed gold nanostructures.

3. Optical properties of gold nanorods

Gold nanorods show unique optical properties depending on the size and the aspect ratio (the ratio of longitudinal-to-transverse length). Although the spherical gold nanoparticle (nanosphere) has only one surface plasmon (SP) band in the visible region, the nanorod has a couple of SP bands. One SP band corresponding to the transverse oscillation mode locates in the visible region at around 520 nm, while the other corresponding to the longitudinal oscillation mode between far-red and near-infrared (near-IR) region. This is the distinctive optical characteristic of the nanorod as compared with the nanosphere. So, nanosphere may have electronic, crystallographic, mechanical or catalytic properties that are different to the nanorods. Such differences may be probed through optical measurements. Spectroscopic measurements are often the easiest methods for monitoring surface processes such as dissolution and precipitation, adsorption and electron transfer. If nanocrystals of any specific geometry could be grown then it is conceivable that optical materials could be designed from scratch. Photonic devices could be created from molecular growth reactors. In the section, we will only describe the optical properties of gold nanorods.

3.1 Plasmon resonance for ellipsoidal nanoparticles

For gold nanorods, the plasmon absorption splits into two bands (Fig. 8) corresponding to the oscillation of the free electrons along and perpendicular to the long axis of the rods (Link and EL-Sayed, 1999). The transverse mode (transverse surface plasmon peak: TSP) shows a resonance at around 520 nm, while the resonance of the longitudinal mode (longitudinal surface plasmon peak: LSP) occurs at higher wavelength and strongly depends on the aspect ratio of nanorods. As aspect ratio is increased, the longitudinal peak is redshifted. To

account for the optical properties of Nanorods, it has been common to treat them as ellipsoids, which allows the Gans formula (extension of Mie theory) to be applied. Gans' formula (Gans, 1912) for randomly oriented elongated ellipsoids in the dipole approximation can be written as

$$\frac{\gamma}{N_p V} = \frac{2\pi\epsilon_m^{3/2}}{3\lambda} \sum_{j=A}^C \frac{(1/P_j^2)\epsilon^2}{\left[\epsilon_1 + \left((1-P_j)/P_j\right)\epsilon_m\right]^2 + \epsilon_2^2} \quad (1)$$

where N_p represents the number concentration of particles, V the single particle volume, λ the wavelength of light in vacuum, and ϵ_m the dielectric constant of the surrounding medium and ϵ_1 and ϵ_2 are the real ($n^2 - k^2$) and imaginary ($2nk$) parts of the complex dielectric function of the particles. The geometrical factors P_j for elongated ellipsoids along the A and B/C axes are respectively given by

$$P_A = \frac{1-e^2}{e^2} \left[\frac{1}{2e} \ln\left(\frac{1+e}{1-e}\right) - 1 \right] \quad (2)$$

$$P_B = P_C = \frac{1-P_A}{2} \quad \text{and} \quad e = \left(\frac{L^2 - d^2}{L^2} \right)^{1/2}$$

Fig. 9 shows the absorbance spectra for gold nanorods with varied aspect ratio calculated using the Gans expressions. The dielectric constants used for bulk gold are taken from the measurements done Johnson and Christy (Johnson, 1972), while the refractive index of the medium was assumed to be constant and same as for H_2O (1.333). The maximum of the longitudinal absorbance band shifts to longer wavelengths with increasing aspect ratio. There is the small shift of the transverse resonance maximum to shorter wavelengths with increasing aspect ratio. Electron microscopy reveals that most nanorods are more like cylinders or spherio-capped cylinders than ellipsoids. However, an analytical solution for such shapes is not derived yet, and so while the results are compared to the formula given by ellipsoids, such comparisons are somewhat approximate (Sharma et al., 2009).

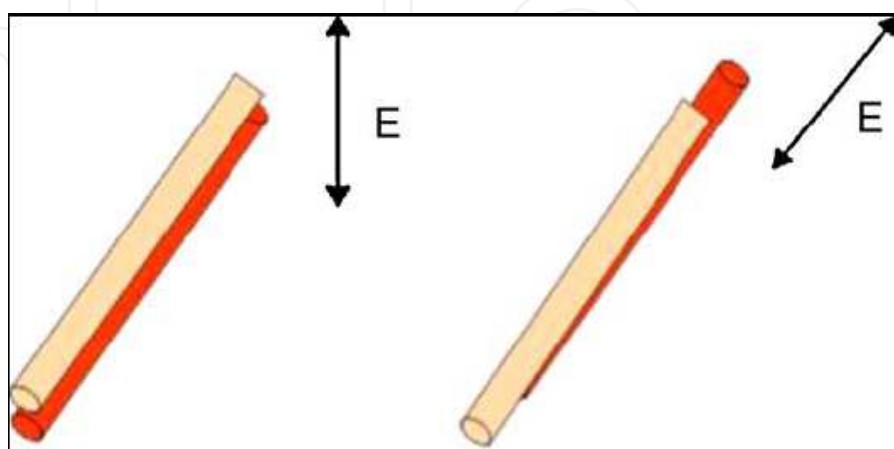


Fig. 8. Transverse and longitudinal modes of plasmon resonance in rod-like particles (Sharma et al., 2009).

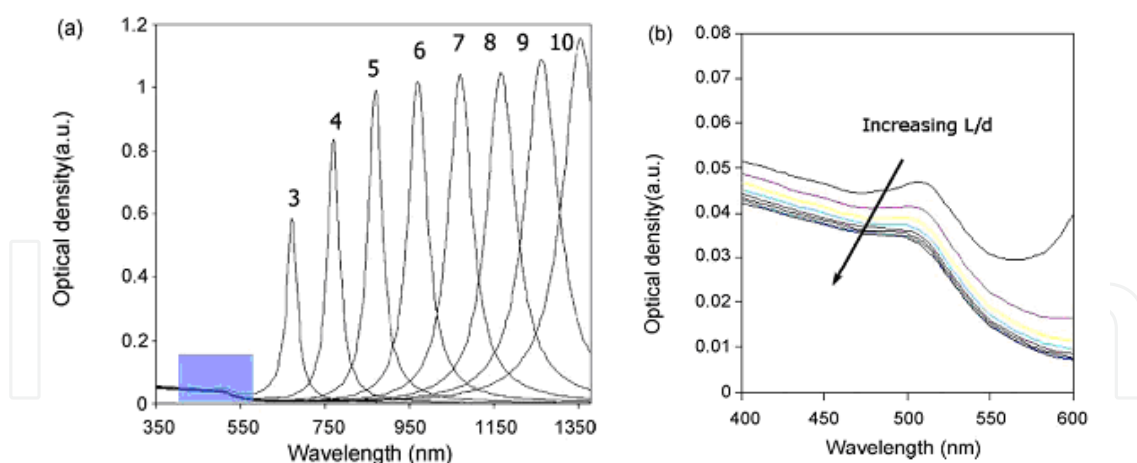


Fig. 9. Absorbance spectra calculated with the expressions of Gans for elongated ellipsoids using the bulk optical data for gold. (a) The numbers on the spectral curves indicate the aspect ratio (L/D). (b) Enlargement of the shaded area of (a) showing slight blue shift of transverse plasmon resonance peak on increasing aspect ratio (Park, 2006).

3.2 Absorption spectrum of colloidal dispersions of gold nanorods

The longitudinal and transverse plasmon resonance can be computed as a function of aspect ratio either by using analytical expression put forth by Gans in 1912 (Gans, 1912) or by using one of numerical techniques (Bohren, 1983; Kelly, 2001). Sharma et al. describe the how the absorption spectrum measured experimentally compares to the results from Gans theory (Gans, 1912; Sharma et al., 2009) and DDA simulations (Kelly, 2001). The gold nanorods cited from their research were synthesized using a seed-mediated method based on use of binary surfactant and all UV-vis-NIR spectra were acquired with a Cary 5G UV-visible-near-IR spectrophotometer. Even though optical properties of pure water were used for calculating the spectrum, the peak resonance measured experimentally show a remarkable agreement with theoretical and simulation results (Fig. 10). Several groups have observed similar trends (Murphy, 2005; Link, 1999).

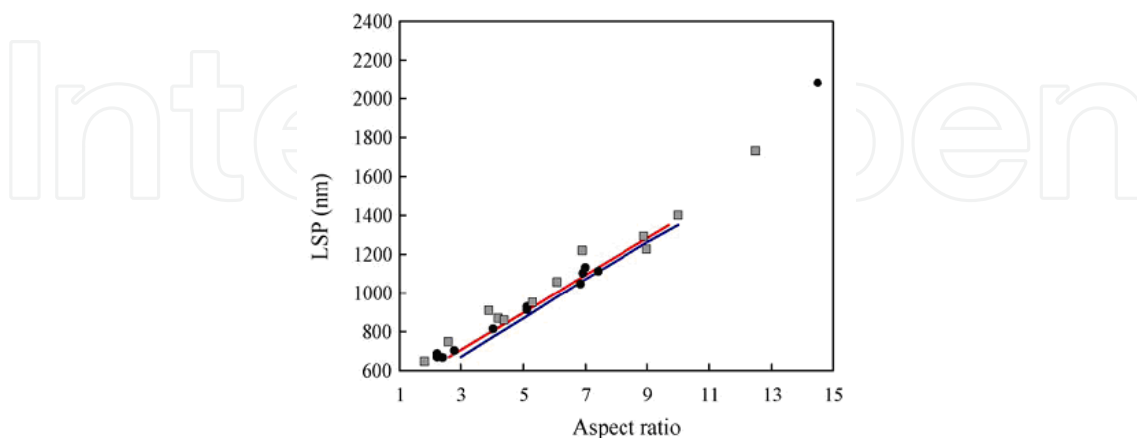


Fig. 10. Longitudinal surface plasmon peak (nm) versus the aspect ratio of nanorods. Simulation results using the DDA method (Kelly, 2003) and the corresponding fit (red straight line) and Gans' calculation (blue straight line). Experimental data from the work (gray squares). Experimental data from our study (black circles) (Park, 2006).

It is well known though that the plasmon resonance is very sensitive to change in the dielectric constant of the medium, and in case of mixed solvents or in sensing applications, this effect must be taken into consideration. Theoretically predicted change in optical properties of colloidal gold suspensions expected upon changing medium has been observed experimentally by several groups (Templeton, 1999; Underwood, 1994). For the gold nanorods, the computed longitudinal plasmon peak increases with an increase in the dielectric constant of medium, as shown in Fig.11. The effect of medium seems more pronounced for longer nanorods, as is evident from the increase in slope observed for higher aspect ratios.

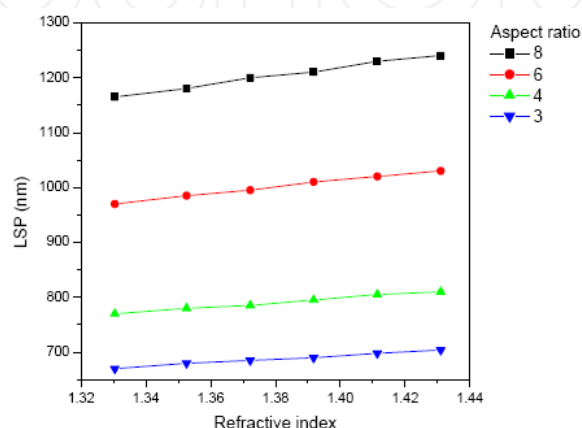


Fig. 11. Calculated LSP as a function of refractive index of medium (Park, 2006).

3.3 Local field enhancements and sensing applications

The electric field is the gradient of potential, and hence using the expression for potential derived earlier, the electric fields inside and outside the sphere are:

$$E_{in} = \frac{3\epsilon_m}{\epsilon + 2\epsilon_m} E_0$$

$$E_{out} = E_0 + \frac{3\bar{n}(\bar{n} \cdot \bar{p}) - \bar{p}}{4\pi\epsilon_0\epsilon_m} \frac{1}{r^3} \quad (3)$$

Resonance in polarizability leads to the resonant enhancement of both the internal and the external dipolar fields. The wavelength at which this resonance occurs depends upon the dielectric function of the metal as well as the medium around it. Since the resonance condition and resulting enhancements of the fields are directly correlated with the shape and size of particle, the basic understanding of this relationship is crucial for their widespread use. The sensitivity of plasmon resonance to the local dielectric environment, implies that any changes within a few nanometers of the particles can be used in say biological or chemical sensing applications (Sharma et al., 2009). For the perfectly spherical particles that can be described by electrostatic approach (Rayleigh limit), only the dipole surface plasmon contributes to the localized enhancement, limiting the overall enhancement achieved. In rod-like particles, highly localized fields can be generated at the tips, providing a much stronger response function for sensing applications. The theoretical and experimental aspects of surface-enhanced Raman scattering and plasmonics based sensing are

widely discussed and debated in literature (Willels, 2007; Maier, 2007) and it forms one of the most anticipated applications of non-spherical gold and noble metal particles.

3.4 Color of colloidal dispersions of gold nanorods

Since the color of colloidal gold depends on both the size and shape of the particles, as well as the refractive index of the surrounding medium, it is important to independently account for the color change of gold nanorod suspension due to presence of either nanospheres or any substance that affects the refractive index of the solvent. Since color of the gold sols is traditionally linked to their shape or size, Sharma et al. characterized the dependence of perceived color on shape and dimensions of the nanoparticles using color science. The color was identified by positioning x and y values in the CIE chromaticity diagram.

This visible light region consists of a spectrum of wavelengths, which range from approximately 700 to 400 nm. For the nanorods, the transverse plasmon resonance peak is not quite as sensitive to the change of aspect ratio, as the longitudinal peak, which shows noticeable shifts in the aspect ratio as seen in Fig.12 which shows the UV-vis-NIR spectrum of gold nanorods dispersions. The relatively intensity of transverse peaks shows that mostly nanorods are present, which were obtained by optimizing synthesis and separation techniques. As predicted by theory, the transverse peak blue shifts with an increasing aspect ratio.

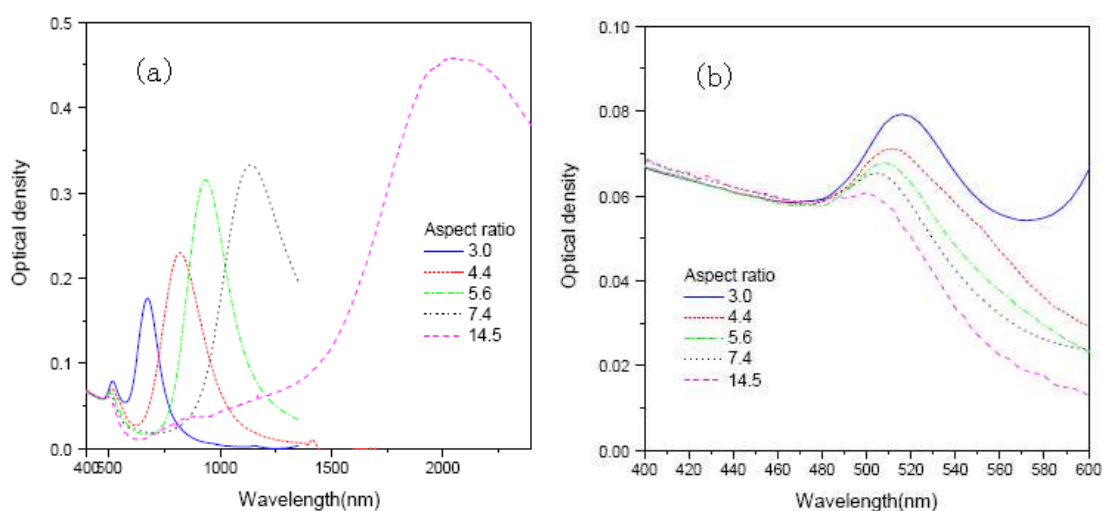


Fig. 12. (a) UV-vis-NIR spectra of dispersions containing gold nanorods with different aspect ratios and (b) transverse peak, showing the blue shift with increase in aspect ratio (Park, 2006).

Fig.13 shows the photograph of the colloidal dispersions of gold nanorods and the color patches simulated using theoretical absorbance data equivalent to the aspect ratio of gold nanorods. The color of solution is basically the same beyond an aspect ratio of around 4. Therefore in a visible region, the dramatic color change cannot be achieved by only changing aspect ratio. But once the longitudinal peak goes beyond 700 nm, (for aspect ratio ~ 3) the change in peak absorption cannot be detected by the human eye and color of gold nanorod dispersion does not change with further increase in aspect ratio. Therefore the color change could be only observed for relatively short range of aspect ratios. But the tunability

of optical properties gold nanorods as a function of aspect ratio provides potentials to use gold nanorods as an optical filter in near infrared region.

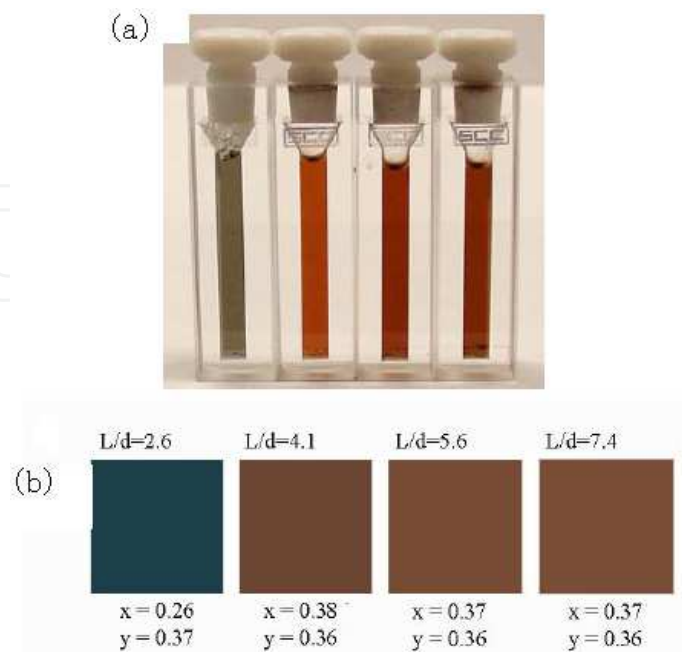


Fig. 13. (a) Photograph of 4 sols of colloidal gold prepared in water. Aspect ratios are 2.6, 4.1, 5.6 and 7.4 (from the left), respectively. (b) The simulated color of dispersion of gold nanorods of different aspect ratio (Park, 2006).

Sharma et al. found that the color in a visible region is rather sensitive to the amount of spherical particles included as byproducts since surface plasmon peak of sphere positions between 500 and 550 nm. Fig.14 shows the color of colloidal dispersion of gold nanorods containing different amount spheres as byproducts. The color changes from purple to brown as the amount of byproducts decreases.

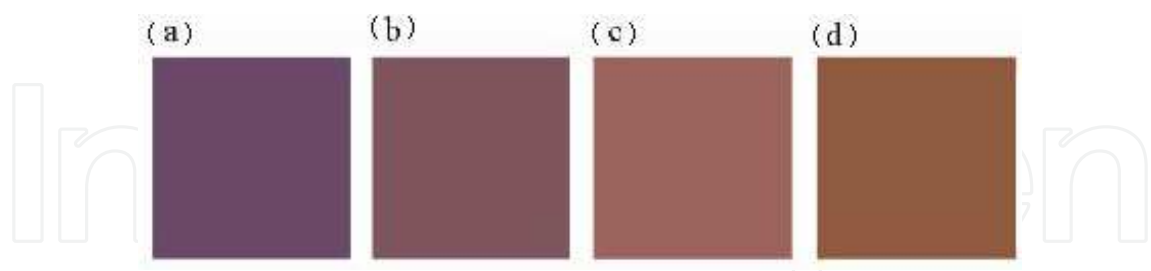


Fig. 14. The color of dispersion of gold nanorods containing different amount of spheres as byproducts: (a) 50 %, (b) 30 %, (c) 10 % and (d) 0 % (Park, 2006).

3.5 Polarization dependent color and absorption in polymer-gold nanocomposite films

The optical properties of gold nanorods are dependent on the state of polarization of incident light, on size and aspect ratio of the particles, and the dielectric properties of the medium. The optical response of a colloidal dispersion of nanorods, as revealed by UV-vis spectroscopy can be thought of as the response from randomly oriented rods. The polarization dependent response of nanorods can be observed by dispersing them in a gel or

polymer matrix, and then stretching the matrix uniaxially, thus aligning the dispersed rods. When the incident light is polarized in the direction of stretching or in the direction coinciding with the average orientation of long axis of nanorods, absorbance is dominated by the response due to the longitudinal resonance. As the angle between the stretching direction and polarization of incoming light is increased, the absorbance shows a marked blue shift. Thus the composite films show a marked polarization dependent color and absorption, making them suitable for use as polarization dependent color filters and for other optical applications (Caseri, 2000; Al-Rawashdeh, 1997).

Caseri (Caseri, 2000) presented a very comprehensive historical perspective and discussion of optical properties of polymer/nanoparticle composites. Caseri and co-workers (Caseri, 2000; Dirix, 1999; Dirix, 1999) found that spherical gold nanoparticles can form “pearl necklace type arrays” by aggregating along the stretching direction and produce dichroic filters that have potential application in creating bicolored displays as illustrated in Fig.15. Al-Rawashdeh (Al-Rawashdeh, 1997) studied the linear dichroic properties of polyethylene/gold rods composites and studied how the local field enhancement could make these composite films impacts the infrared absorption of probe molecules attached to the surface of nanorods.

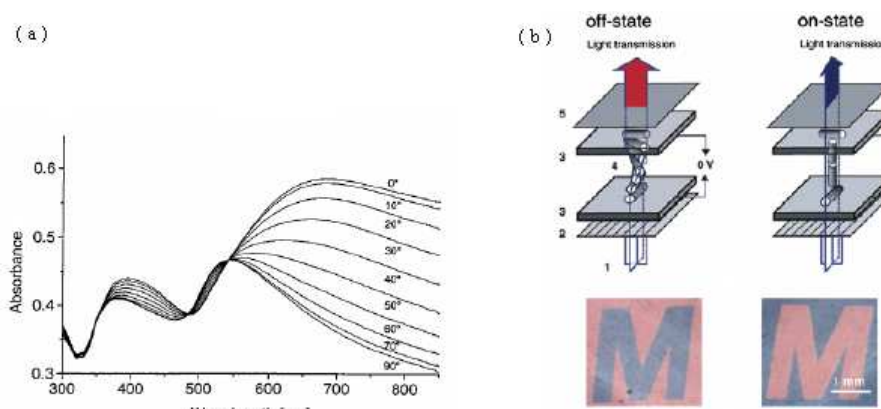


Fig. 15. (a) UV-vis spectra of uniaxially stretched films of high-density polyethylene/gold composites. The angle on spectra indicates the angle between the polarization direction of the incident light and the drawing direction. (b) Twisted nematic liquid crystal displays (LCD) equipped with a drawn polyethylene-silver nanocomposite. The “M” represents the on state, the drawing direction is in the picture above parallel and below perpendicularly oriented to the polarizer (Caseri, 2000; Park, 2006).

The transmittance spectra as a function of polarizer angle are shown in Fig.16 for a nanocomposite with gold nanorods of aspect ratio 2.8, and draw ratio of 4 was used for this study. The longitudinal plasmon resonance blue shifts as polarization angle is increased, and the intensity of the peak drops, in accordance with the observations by other groups (Caseri, 2000) (Fig. 17).

Sharma et al. obtained transmittance spectra at different polarizer angles and calculated extinction ratio, $E.R. = 10 \log_{10}(T_{\perp}/T_{\parallel})$ [dB] where T_{\perp} and T_{\parallel} are the transmittance perpendicular and parallel to the stretching direction, respectively. Maximum extinction ratio (Park, 2006) is 18 dB at $\lambda = \lambda_{LSP}$ and is comparable to those previously reported in the literature (Matsuda, 2005). The thickness of the film is $50 \mu\text{m}$ and it has good flexibility.

When the aspect ratio of nanorods is sufficiently large, the LSP shifts to the near-IR region. This indicates that the wavelength region displaying optical dichroism can be shifted from the visible to the near-IR. This enables the fabrication of thin film optical filter that respond to the wavelengths in the near-IR region (Fig.18).

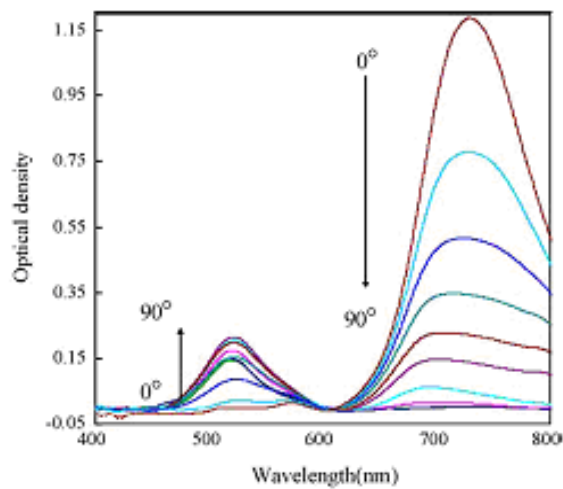


Fig. 16. UV-vis-NIR spectra of PVA/ gold nanorods nanocomposites for varying polarization angles L/D of gold Nanorods is 2.8 (Park, 2006).



Fig. 17. Optical micrographs of drawn PVA-gold nanocomposites (4 % w/w gold, draw ratio 4): (a) unpolarized, polarization direction, (b) parallel and (c) perpendicular to the drawing direction. Scale bar is 50 mm (Park, 2006).

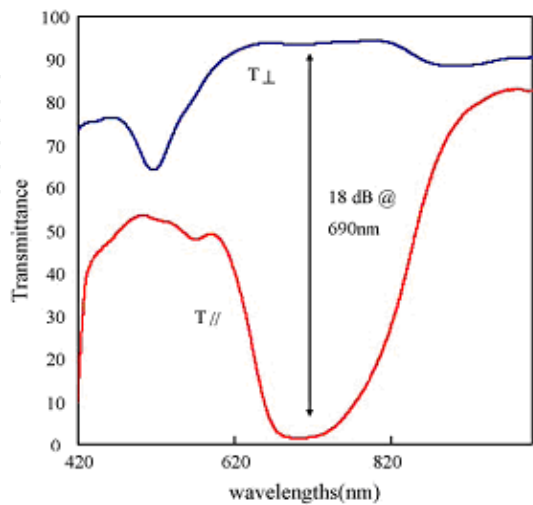


Fig. 18. UV-vis-NIR spectra of PVA/ gold nanorods nanocomposites for varying polarization angles L/D of gold Nanorods is 2.8 (Park, 2006).

4. Conclusion

In metal nanomaterial research, the optical properties have been of interest especially because of the applications to medical diagnostics and nanooptics. Gold nanoparticles are attracting great attention due to their unique optical that is dependent on their size and shape. In spherical gold nanoparticles, the plasmon absorption is red shifted with an increase in the diameter of the nanoparticle. Gold nanorods show different color depending on the aspect ratio, which is due to the two intense surface plasmon resonance peaks. The color change provides the opportunity to use gold nanorods as novel optical applications. There have been many applications utilizing this intense color and its tunability (Pérez-Juste et al., 2005). One of them is in the field of biological system. Nanorods bind to specific cells with greater affinity and one can visualize the conjugated cell using a simple optical microscope due to the enhanced scattering cross section (El-Sayed, 2005). This is how gold nanorods are used in molecular biosensor for the diagnosis of diseases such as cancer. Nanorods show enhanced fluorescence over bulk metal and nanospheres, due to the large enhancement of the longitudinal plasmon resonance (Eustis, 2005), which will prove to be beneficial in sensory applications. All these properties make gold nanorod a good candidate for future nanoelectronics, once appropriate techniques allow for the generation of artificial structures in 2D or 3D (Park, 2006).

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6. References

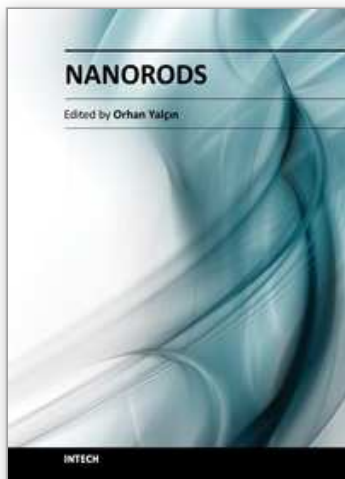
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