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Time dependence of the surface plasmon resonance of copper nanorods

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Abstract
Copper nanorods have been synthesized by electrodeposition with different lengths in porous polycarbonate (PCT) membranes with a pore diameter of 50 nm and a thickness of 4 μm. The PCT membranes were dissolved in dichloromethane (CH_2Cl_2) and the solvent was replaced by methanol solutions. Extinction peaks at 587, 581 and 574 nm were observed for the Cu nanorods with aspect ratio $R = 6, 8$ and 10 in methanol, respectively. Polarization of the molecules of the medium around the wires changes the dielectric constant of the medium. Hence, the wavelength of the extinction peaks does not shows good agreement with calculations that were done on basis of Gans' theory with nominal dielectric constant of the medium. In this study, the effective medium dielectric constant for Cu nanorods in methanol was obtained by comparing the experimental data and calculation results. The effective medium dielectric constant (ε_m^{eff}) for the Cu nanorods in methanol was decreased by increasing the aspect ratio of the nanorods. After one week, CuO or Cu_2O shells with about 20 nm radius were observed around the copper nanorods and so the contemporary peak wavelength was shifted to red. In this case, variation of the shell's diameter with time caused the change in value of ε_m^{eff}. It was found for the Cu nanorods that the value of ε_m^{eff} increased with time.

1. Introduction

In recent years, metal nanowires and nanorods have been extensively investigated due to their interesting electronic and optical properties and potential applications in nanodevices. Applications might be developed in various fields such as field-emission emitters, magnetic storage devices, interconnects and biochemical sensors [1–4]. For some of these applications,

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the nanostructures must have a high electrical conductance, and hence copper is a good choice. Metallic nanostructures show interesting optical properties; for example, suspensions of metal nanoparticles show different colors depending on their size. Mie was the first to explain this phenomenon theoretically in 1908 by solving Maxwell's equation for the absorption and scattering of electromagnetic radiation by spherical particles [5]. The physical origin of light absorption by metallic nanostructures is the coherent oscillation of the conducting band electrons induced by the interacting electromagnetic field. These resonances are known as surface-plasmon resonances (SPRs). According to Mie's model, the total extinction coefficient (cross-section) of small metallic particles is given as the summation over all electric and magnetic multipole oscillation contributing to the absorption and scattering of the interacting electromagnetic field. To calculate the light absorption of non-spherical metallic particles, the orientation with respect to the oscillating electric field must be taken into account. However, an *exact* analytical solution for cylindrical shapes is not possible. In 1912, Gans derived the extinction cross-section for nanorods, when the dipole approximation holds [6]. The optical properties of copper nanorods are of great interest due to the strong surface plasmon resonance absorption in the visible region of the electromagnetic spectrum and high electrical conductivity.

In recent years, many papers have been published on the SPR of noble and highly conductive nanowires and nanorods. For example, Zong considered the SPR of Cu nanorods [7]. In most articles, Gans' theory is widely used because this theory predicts the wavelength of absorbance peaks very well [8].

One simple and versatile approach to prepare metal nanorods is the template method. The most suitable templates for metal nanowires and nanorods include cylindrical narrow pores of polycarbonate track-etched (PCT) membranes, anodic aluminum oxide (AAO) templates and nanoporous mica [9–11]. The PCT template is an ideal template, because it has tunable pore dimensions over a wide range of diameters and shows better wetting properties than that of the AAO template.

In this study, copper nanorods were made electrochemically in a PCT template and then were dispersed in liquid phase. The ageing time becomes important when nanostructures are exposed to active media. In this condition, the properties of nanostructures change gradually with time due to chemical and physical interaction. We discuss how the aspect ratio and ageing time have effects on the properties of the medium dielectric constant and hence on the SPR of copper nanorods.

2. Experimental details

The arrays of the Cu nanorods were obtained by electrodeposition of copper inside the pores of commercial polycarbonate track-etched membranes (Whatman). The polycarbonate membranes had a thickness of about 4 μm and pore diameter of 50 nm, respectively. The growth of nanorods was performed at room temperature in a sulfate solution containing Cu^{2+} ions with a pH of 3. Before electrodeposition, a thin film of gold of about 50 nm thickness was deposited on the back side of PCT templates by the sputtering technique, serving as a working electrode. The electrolyte used for electrodeposition of the Cu nanorods had the following composition: 0.2 M $CuSO_4{\cdot}5H_2O$ and 0.4 M H_3BO_3.

Nanorods were deposited using an EG&G potentiostat, in a conventional three-electrode cell. A saturated calomel electrode (SCE) was used as a reference electrode for the applied potential. Moreover, a Pt plate was used in electrolyte solution as the counter-electrode. The current versus time of deposition was used to control the nanorods' length and to stop the deposition process before the nanorods reached the surface of the membranes. In order to study

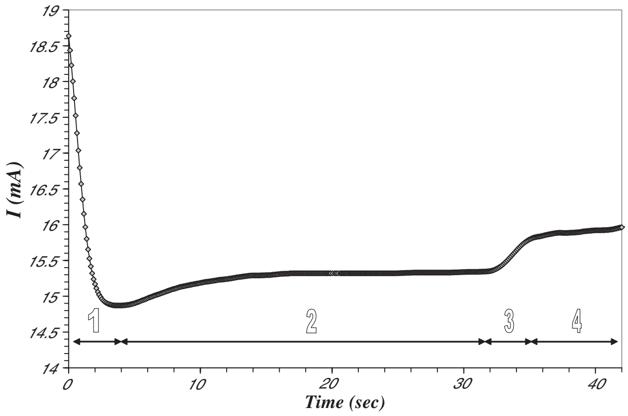

Figure 1. A typical current transient curve, during electrodeposition at a constant potential of −1 V.

the effect of the medium on the SPR of the Cu nanorods, the PCT membrane was dissolved in dichloromethane (CH_2Cl_2), and after filtration the solution was replaced by methanol. The optical absorption of dispersed copper nanorods was studied by visible near-infrared (vis/NIR) spectroscopy. Selected area electron diffraction (SAED), energy-dispersive x-ray (EDX) and transmission electron microscope (TEM) analyses were used to characterize the structure, composition and aspect ratio (R) of the nanorods.

3. Results and discussion

Growth of Cu nanorods in pores of PCT membranes was studied by I–t curves (chronoamperometry experiments). Figure 1 shows a typical current transient curve obtained during electrodeposition at a constant potential of −1 V.

The current response during reduction of the Cu^{2+} ions at a constant potential depends on the mass transport condition and effective surface area of the working electrode (PCT membrane). The I–t curve may be separated into four different stages. At the initial time of deposition, the current decreases due to mass transport limitation (stage 1). In stage 2, the metal is growing inside the pores and a slightly increasing current is observed, as shown in figure 1. When the pores are filled and the wires reach the top of the membrane surface, the effective surface area of the cathode is increased and so an increasing deposition current can be observed (stage 3). In this stage hemispherical caps originate from each nanorod, because of three-dimensional depositions. These hemispherical caps reach each other and form a continuous film with further deposition; hence the surface area of the cathode remains constant and the current saturates at stage 4. In this work, the electrodeposition process was cut off in stage 2 at $t = 7, 9$ and 11 s. Hence Cu nanorods were obtained with different lengths but the same diameter.

For TEM observations a drop of solvent was released on a carbon-covered nickel grid and allowed to evaporate in air. A typical TEM image of copper nanorod is shown in figure 2(a) for $t = 7$ s deposition. The average size of the rods is observed to be about 300 nm length and 50 nm diameter, which means that the aspect ratio is about 6. The selected area electron diffraction (SAED) pattern for an individual copper nanorod is shown in figure 2(b). The pattern exhibits a crystalline structure that can be related to a hexagonal lattice. However, after one week, the TEM image of the same sample showed narrow lines in the center of each rod, as

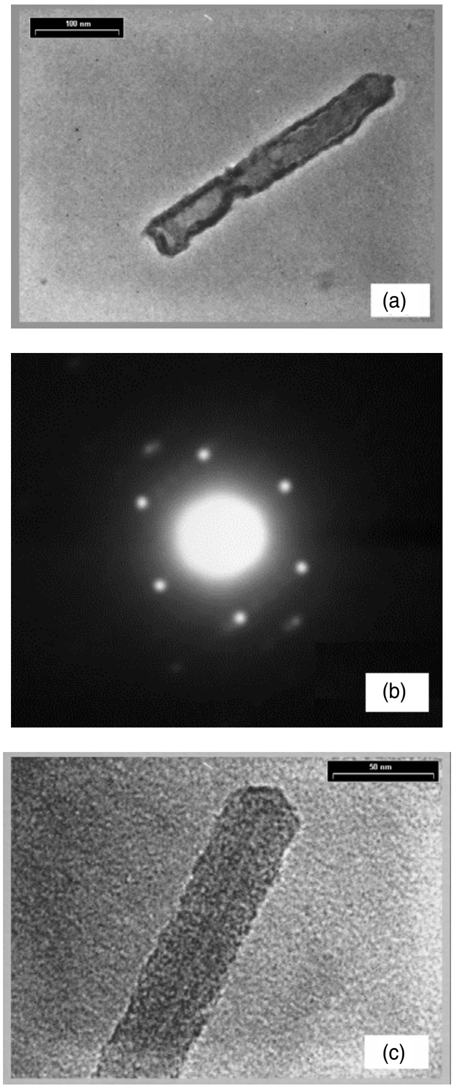

Figure 2. TEM image of a copper nanorod after $t = 7$ s deposition ($R = 6$): (a) as deposited, (b) the selected area electron diffraction (SAED) pattern for an individual copper nanorod, (c) TEM image of copper nanorod after one week. The core and shell layer have a radius about 5 and 20 nm, respectively.

shown in figure 2(c). The different contrast in the center and wall of each rod exhibits different compositions for the core and the shell layer. This can be attributed to oxidation of rod's surface and formation of the CuO or Cu_2O shell. In this image, the core and shell layer have a radius of about 5 and 20 nm, respectively. Energy-dispersive x-ray (EDX) experiments on the samples show that the copper and oxygen concentrations are about 21% and 52%, respectively. The excess oxygen is due to physical absorption of oxygen from the environment.

The ultraviolet–visible (UV–vis) spectra of copper nanorods with different aspect ratio dispersed in methanol are shown in figure 3. The lengths of these nanorods are proportional to the time of deposition. Extinction peaks at 587, 581 and 567 nm are observed for Cu nanorods

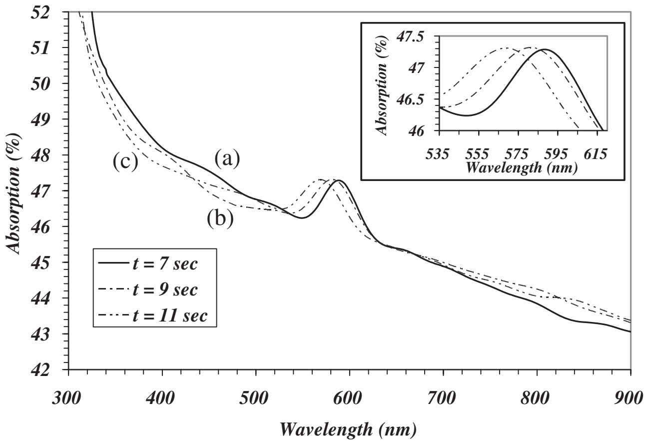

Figure 3. Optical absorption spectra of the Cu nanorods grown for (a) $t = 7$ s ($R = 6$), (b) $t = 9$ s ($R = 8$) and (c) $t = 11$ s ($R = 10$). The inset shows detail of extinction peak.

with $L = 300, 400$ and 500 nm, respectively. It is clearly observed that by increasing the aspect ratio, the extinction peak shifts to blue. The full widths at half maximum (FWHMs) for these peaks are approximately identical, indicating similar size distributions of nanorods. Experimental optical absorption of the copper nanorods dispersed in methanol is compared with the results of Gans' theory.

Details of Gans' theory can be found in [12]. According to Gans, the extinction coefficient γ for N particles with volume V is given by the following equation.

$$\gamma = \frac{2\pi N V \varepsilon_{\mathrm{m}}^{3/2}}{3\lambda}\left[\frac{\frac{2}{p_x^2}\varepsilon_2}{(\varepsilon_1 + k_x\varepsilon_{\mathrm{m}})^2 + \varepsilon_2^2} + \frac{\frac{1}{p_z^2}\varepsilon_2}{(\varepsilon_1 + k_z\varepsilon_{\mathrm{m}})^2 + \varepsilon_2^2}\right] \tag{1}$$

where λ is the wavelength of light, ε_{m} the dielectric constant of the medium, ε_1 and ε_2 are the real and complex parts of copper dielectric function related to interacting light and K_i ($i = 1, 2, 3$) are screening parameters.

In this theory, for each dimension a geometrical factor (P_i) is given by

$$p_z = \frac{1-e^2}{e}\left(\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right) - 1\right) \tag{2}$$

$$p_x = p_y = \tfrac{1}{2}(1 - p_z) \tag{3}$$

$$e = \frac{\sqrt{L^2 - d^2}}{L} \tag{4}$$

where L and d are the nanorod's length and diameter, respectively. For each dimension the screening parameter is

$$K_i = \frac{1}{p_i}(1 - p_i)\,. \tag{5}$$

Here K_i ($i = 1, 2, 3$) are the same as K_X, K_Y and K_Z in equation (1). The resonant condition for nanorods is given by

$$\varepsilon_1 = -K_i\varepsilon_{\mathrm{m}}. \tag{6}$$

In equation (1), when the denominators of the first and second terms are minimum, where $ki = kx, kz$, the extinction coefficient (γ) shows two peaks. These peaks are known as the

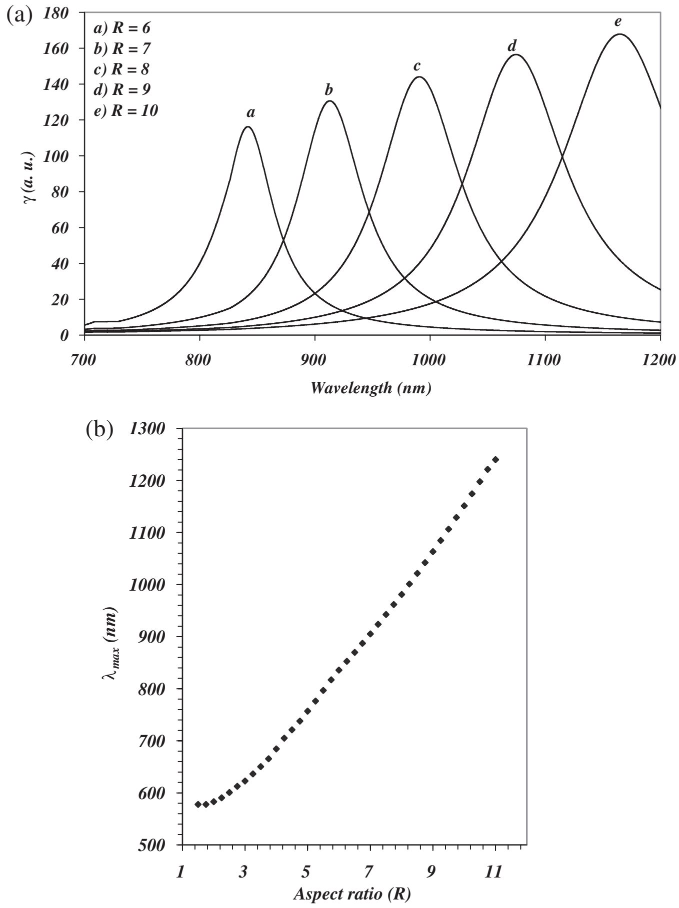

Figure 4. (a) Calculated extinction coefficient for methanol nominal dielectric constant, with the aspect ratio ranging from $R = 6$ to 10, (b) theoretical calculation of the longitudinal resonance wavelength at different aspect ratios of copper nanorods in methanol.

transverse and longitudinal peaks. In such condition, the conduction band electrons on the surface of nanorods oscillate with the same frequency as the incident electromagnetic field and therefore resonance conditions appear. These resonances are known as surface plasmon resonances.

The calculated extinction coefficient for the nominal dielectric constant of methanol is presented in figure 4(a), when the aspect ratio is varied from $R = 6$ to 10. The values of ε_1 and ε_2 for bulk copper and the dielectric constant of the medium are obtained from [13]. As shown in this figure, an increase of the aspect ratio (R) causes an increase of the peaks' wavelength (λ_{max}) and height of the peaks (γ_{max}). The surface plasmon resonance wavelength as a function of copper nanorod aspect ratio in methanol is shown in figure 4(b). A linear correlation is observed from $R = 4$ to 11, but for high aspect ratio values, Gans' theory predicts a slow curvature. The calculated extinction coefficient shifts to red by increasing the aspect ratio, and this is in contrast to the observed blue shifts in figure 3.

It should be mentioned that copper nanorods are extremely sensitive to the dielectric properties of their environment. One possible reason for such a variation is the alteration of

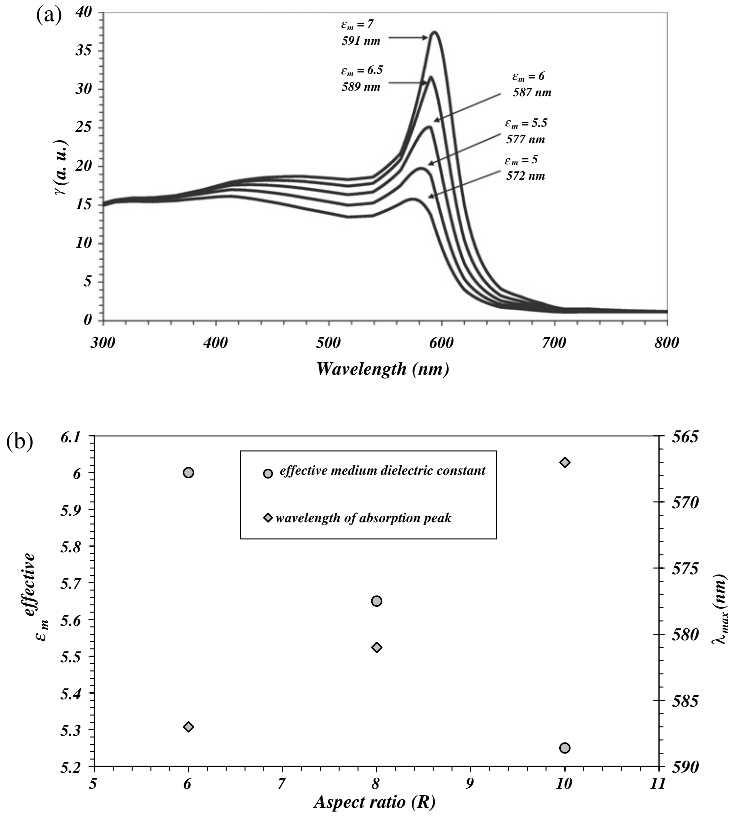

Figure 5. (a) The calculated extinction coefficient versus wavelength for different solvent dielectric constant and aspect ratio $R = 6$, (b) the calculated effective medium dielectric constant for three aspect ratios of Cu nanorods and the observed wavelength of the absorption peak.

the dielectric constant of the medium in the vicinity of the Cu nanorods. This is may be due to polarization of molecules of the medium around the rods. For example, El-Sayed and co-workers proposed that the polarized water layers around Au rods have a substantially higher refractive index than that of water [14]. Hence, the dielectric constant of the medium is higher than the nominal dielectric constant.

On the other hand, it is known that it is not possible to match experimental results with calculation for a single value of the dielectric constant of the medium when the aspect ratio varies. For example, Link and co-workers [14] show that this discrepancy can be resolved only if the dielectric constant of the medium becomes a function of the aspect ratio. They found that if the dielectric constant of the medium increases in a nonlinear way with decreasing aspect ratio, the calculation will match experimental data [14].

Therefore, we tried to find the effective medium dielectric constant ($\varepsilon_{\mathrm{m}}^{\mathrm{eff}}$) for Cu nanorods in methanol, experimentally. In this case, the aspect ratios are obtained from TEM images and the dielectric constant of the medium is assumed as an indeterminate parameter. Then extinction coefficients are plotted for the different values of ε_{m}. A plot of the calculated extinction coefficient versus carrier dielectric constant is shown in figure 5(a), when the aspect ratio is kept fixed at a value of $R = 6$. It is worth noting that the peak wavelength increases as ε_{m} increases, but the peak width decreases. By comparing figures 5(a) and 3, it is found that

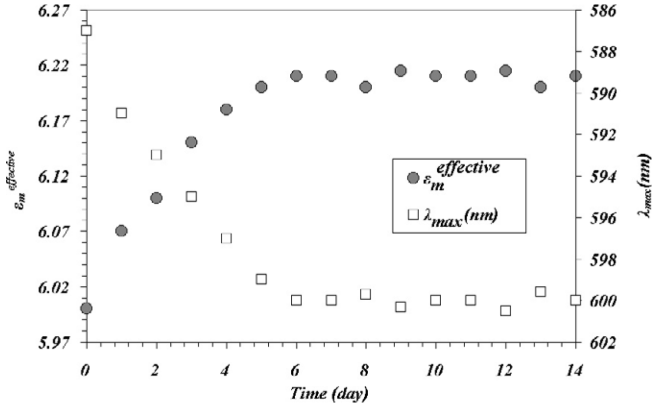

Figure 6. Time dependence of the effective medium dielectric constant for Cu nanorods ($R = 6$) in methanol and wavelength of the absorption peak.

$\varepsilon_{\rm m} = 6$ shows the best agreement for copper nanorods with $R = 6$, and hence this value is accepted as the effective medium dielectric constant for this aspect ratio.

The calculated effective medium dielectric constants for samples with different aspect ratios are shown in figure 5(b). This value decreases from 6 to 5.25 for Cu nanorods in methanol when the aspect ratio increases from 6 to 10.

As mentioned before, the nanorods oxidize over time and a shell layer of CuO or Cu_2O appears. The thickness of the shell changes with time and so the effective dielectric constant of the medium varies. It is noticeable that the theory of the core–shell nanorods is complex and sensitive to the dielectric constant and thickness of the shell layer. But the dielectric constant generally has a gradual change in shell layer, and an exact determination of the shell layer is very difficult due to its change with time. On the other hand, the effect of the thin non-absorbing shell is similar to the effect of immersion in a medium with the same refractive index. Hence, we used the above process to determine the change in effective medium dielectric constant with time. The result for $\varepsilon_{\rm m}^{\rm eff}$ for the Cu nanorods with $R = 6$ is shown in figure 6. With increasing time, the values of peak wavelength and $\varepsilon_{m}^{\rm eff}$ increase due to an increase in the shell diameter, but these values saturate after one week. In summary, this graph emphasizes that the optical properties of copper rods in a liquid phase change with time, and hence the ageing time must be accounted for as a parameter in the optical properties.

4. Conclusion

The absorption spectra of colloidal solutions of copper nanorods in methanol show that the absorption peak blue-shifts on increasing the nanorods' aspect ratio. The calculated extinction coefficient on the basis of Gans' theory and with nominal dielectric constant of the medium is in contrast with the absorption spectra that have shown blue shifts with increasing aspect ratio. However, polarization of the molecules of the medium around the nanorods or the existence of a CuO or Cu_2O shell around the Cu nanorods alters the $\varepsilon_{\rm m}$.

In order to find the effective medium dielectric constant, we considered that the aspect ratios could be obtained from TEM images and assumed the dielectric constant of the medium to be an indeterminate parameter. By comparing calculation results and experimental data, the value for $\varepsilon_{\rm m}^{\rm eff}$ was determined for various aspect ratios of Cu nanorods in methanol. This value decreases with increasing aspect ratio of the nanorods. The effect of ageing on the surface plasmon resonance of the Cu nanorods is shown by the fact that, with time, the peak wavelength shifts to red, and it is found that the value of $\varepsilon_{\mathrm{m}}^{\mathrm{eff}}$ increases with time.

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