Vol 11 No 12, December 2002
1009-1963/2002/11(12)/1307-06

Chinese Physics

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Fabrication and optical properties of platinum nanowire arrays on anodic aluminium oxide templates*

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(Received 17 April 2002; revised manuscript received 12 August 2002)

Arrays of Pt nanowires, fabricated by electrodepositing Pt metal into nanoporous anodic aluminium oxide (AAO) templates, exhibit a preferable optical absorption band in the ultraviolet-visible (UV-VIS) spectra and present a blueshift as the wire aspect ratio increases or its radius decreases. This type of optical property of Pt nanowire/porous alumina composites has been theoretically explored using Maxwell–Garnett (MG) effective medium theory. The MG theory, however, is only applicable to nanowires with an infinitesimally small radius relative to the wavelength of an incident light. The nanowire radius is controlled by the pore radius of the host alumina, which depends on anodizing conditions such as the selected electrolyte, anodizing time, temperature and voltage. The nanowire aspect ratios depend on the amount of Pt deposited into the nanopores of AAO films. The optical absorption properties of the arrays of Pt nanowires with diameters of 24, 55 and 90 nm have been investigated by the UV-VIS spectra, which show that the extinction maximum (λ_{max}) shifts to shorter wavelength side as the wire aspect ratio increases or its radius decreases. The results are qualitatively consistent with those calculated based on the MG theory.

Keywords: Pt nanowire arrays, Maxwell–Garnett theory, blueshift, electrodeposition
PACC: 8140T, 8280F, 8160T, 0565

1. Introduction

Nanomaterials,[1] especially many nanocomposite materials, have attracted a great deal of interest in the last twenty years. One of the most important aspects concerns the optical properties of nanocomposite membranes containing metal nanowires embedded in the pores of anodic aluminium oxide (AAO) templates.[2]

Optical properties of nanocomposite materials are different from those of the bulk materials.[3] One of the different phenomena is the blueshift, which is generally explained by two types of effects. The first, the quantum size effect, originates from the widened energy gap as the size of the wire decreases. Ball and Garwin[3] thought that the energy gap between molecular orbit levels occupied and unoccupied by electrons increases with decreasing wire diameter. The other is the surface effect,[4] in which the surface tension leads to the lattice distortion and lattice constant reduction, namely, the reductive bond length engenders an increase in vibration eigenfrequency of the nanoparticle bond, and then causes the infrared absorption band to shift to greater wavenumbers. By investigating the optical properties of nanocomposite membranes, we can consider theur applications, such as surface-enhanced absorption, Raman spectrum, chemical catalyses and chemical sensors.

Andersson *et al*[5] derived the optical properties of the Ni-pigmented AAO by using the MG theory[6,7] and the Bruggeman theory.[6,8] They investigated the optical reflectance by both experimental measurement and theoretical calculation. The latter yielded a result which is in quantitative agreement with the measured spectral reflectance. Aspness *et al*[9] studied the microstructure of the Pt/InP/$HClO_4$ system and pro-

*Project supported by the Gansu Natural Science Foundation, the Key Teacher Foundation, and the Research Foundation for Scholars from Abroad, the latter two being from the Ministry of Education, China.

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posed that it could be for photoelectrochemical conversion within the effective medium theory, limit theorem, and suitable laminar approximations. The optical properties of composite membranes containing arrays of nanoscopic Au cylinders show that the composite membranes are transparent in the infrared (IR) portion of the electromagnetic spectrum but opaque in both near IR (NIR) and visible regions.[10] The results are in agreement with the prediction of the MG theory. According to this theory, the optical transparency occurs when the metal cylinders are isolated from each other, because the photon fields induce a screening depolarization charge on the surface of the metal cylinders that prevents the fields from penetrating into the metal. More recently, Huber *et al*[11] have presented a self-consistent model that allows for evaluation of the properties of electromagnetic fields propagating along the wire length. At the same time, for the self-assembled arrays, Huber *et al* verified experimentally that the velocity of propagation in the array is equal to the velocity of light in free space.

However, the previous works have mainly focused on films and nanoparticles fabricated with commercial membranes. Unfortunately, the optical properties of nanowires embedded in these membranes have been addressed before, and the available materials are not especially suited to this research because the membrane cannot ideally control the size and aspect ratio of the nanowires. In this paper, we describe the fabrication of Pt nanowires with very long aspect ratios via AAO membranes and the measurements of their morphology, crystal structure and optical characteristics. Meanwhile, the experimental optical results are compared with the calculated results based on the MG theory.

2. Experiment

The preparation of Pt nanowire arrays is similar to that described in Refs.[16]–[20]. Briefly, a high purity (99.997%) Al sheet ultrasonically degreased in tricholoroethylene and etched in NaOH solution was electropolished for 3 min in a mixed solution of $C_2H_2O_6$ and $HClO_4$ (volume ratio = 4 : 1). Then it was anodized in different acidic solutions for 60 min. In this work, the AAO templates were obtained with pore diameters of 24, 55 and 90 nm when using 1.2mol sulfuric acid, 0.6mol oxalic acid and 0.5mol phosphoric acid as cathode, separately. The arrays of Pt nanowires, with 1.5μm long, were prepared by electrodepositing Pt into different AAO templates. The Pt atoms were electrodeposited into the AAO templates from an aqueous solution containing platinum chloride and boric acid with pH= 3.0. The electrodepositions were all conducted at 200Hz and 12V AC voltage at room temperature for a duration of 5 min in different acidic solutions. The AAO films filled with nanowires were removed from the Al substrates using aqueous $HgCl_2$. The nanowires were liberated from the AAO films by dissolving the alumina layer with aqueous NaOH.

In this study, transmission electron microscopy (TEM) was used to determine the topography, diameter and length of the Pt nanowires. The crystal structure of nanowires was obtained using x-ray diffraction (XRD) and selected-area electron diffraction (SAED).

3. Results and discussion

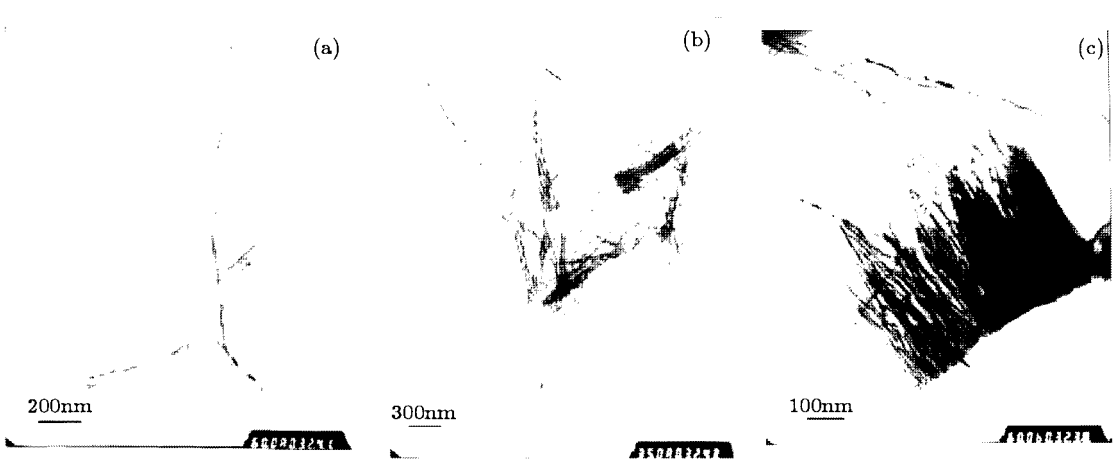


Fig.1. TEM images of Pt nanowires liberated from alumina templates: (a) TEM photograph of a localized spot 60 000×; (b) TEM photograph, 35 000×; (c) TEM photo, 50 000×.

Figure 1 shows the TEM image of Pt nanowires prepared as mentioned above. It reveals that the Pt nanowires are both very regular and uniform with an average of 1.5 μm in length and 24 nm in diameter. The diameter increases to 55 nm in oxalic acid solution, and to approximately 90 nm when phosphoric acid is used.

Figure 2 shows the XRD patterns of the AAO film filled with Pt nanowires and an electron diffraction pattern of a single Pt nanowire. These exhibit that every Pt nanowire is composed of some Pt single crystals and the lattice is of a face-centred-cubic (fcc) structure from Fig.2(b). This is identical to the structure of the bulk Pt metal.

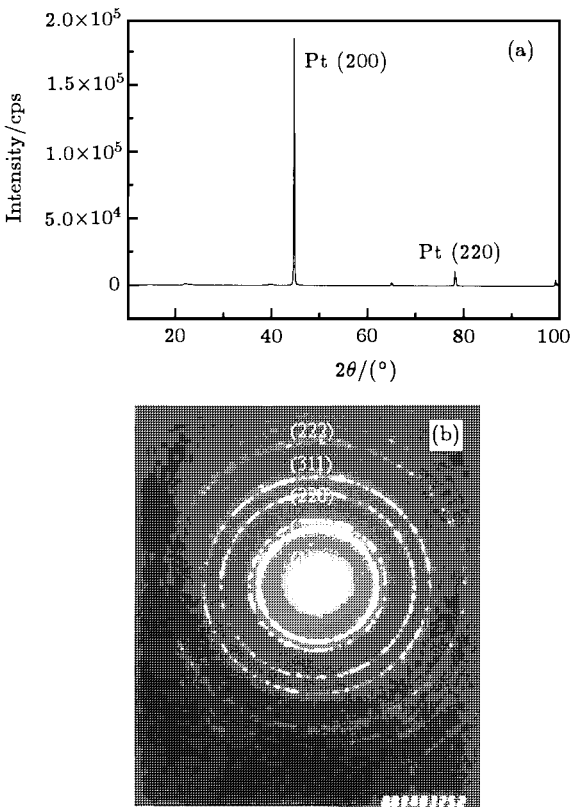


Fig.2. (a) XRD pattern of Pt nanowires embedded in AAO films; (b) SAED photograph of a Pt nanowire.

In Fig.3(a) UV-VIS absorption spectra for composites containing Pt nanowires with different radii are plotted. These spectra indicate that the wavelength of maximum extinction increases with increasing nanowire radius, resulting in colour variations of the composites. As a result, we may observe that the composite membranes are transparent in the IR portion of the electromagnetic spectrum but opaque in both the NIR and VIS regions. For the same reason, the films anodized by phosphoric acid are blue in the VIS regions. However, it is hard to vary the colour of films anodized by oxalic acid and the variation of colour could not be observed at all for films anodized by sulfuric acid at room temperature. Figure 3(b) shows the absorption spectra calculated using the MG theory. We found that $\lambda_{\max}$ shifts to shorter wavelengths as the pore diameter of the film decreases, which is in agreement with the experimental data in Fig.3(a).

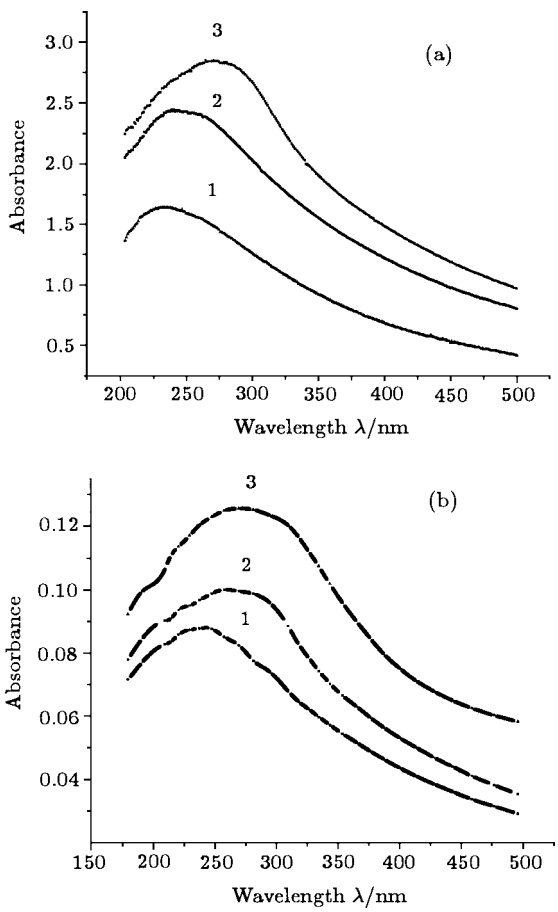


Fig.3. UV/VIS absorption spectra for the composite membranes containing Pt nanowires with different diameters: (a) experimental results; (b) calculated results from MG theory (curve 1, $k = 1$, $f_m = 0.048$, $2b = 24$ nm; curve 2, $k = 1$, $f_m = 0.06$, $2b = 55$ nm; curve 3, $k = 1$, $f_m = 0.1$, $2b = 90$ nm).

In order to test the above consistency in experimental and theoretical results, the following section will account for the calculation procedure from the MG theory, which is given by

$$\frac{\varepsilon_c - \varepsilon_h}{\varepsilon_c + k\varepsilon_h} = f_m \frac{\varepsilon_m - \varepsilon_h}{\varepsilon_m + k\varepsilon_h}. \qquad (1)$$

The dielectric constant of the composite membrane ε_c is related to the dielectric constants of the metal nanowires ε_m and the host matrix ε_h. Here, f_m is

the volume fraction of the metal in the composite membrane, k is the screening parameter that depends on the shape of the nanowires, usually, $1 \leq k \leq 2$ for spherical particles and nanowires. According to Eq.(1), ε_c can be expressed by ε_m, ε_h, f_m, and k. From the knowledge of the four constants, we can readily derive the optical constants n_c, and k_c of the composite membrane filled with metal can also be calculated via

$$\varepsilon = (n + iK)^2 = n^2 - K^2 + i2nK, \qquad (2)$$

where n and K denote the refractive index and absorption coefficient, respectively. The term K should not be confused with the screening parameter in Eq.(1). The ε_m value depends on optical constants n_m and k_m taken for Pt from the Handbook of Optical Constants of Solids.[12] The total transmittance $T_{\rm tot}$ [13] is given by

$$T_{\rm tot} = \left[1 - \frac{(n_c - 1)^2 + k_c^2}{(n_c + 1)^2 + k_c^2}\right] \exp(-4\pi k_c d/\lambda), \qquad (3)$$

where d is the thickness of the composite membrane and λ is the incident wavelength. According to Eq.(2), for the transmittance of the host matrix, n_o and k_o can be gained from the slope and from the y-intercept by plotting the natural logarithm of the total transmittance $\ln(T_{\rm tot})$ versus the membrane thickness d. However, experimental n_o and k_o are the constants of the composite containing alumina and air in the pores. The Bruggeman approximation,[14] another type of effective medium theory, is used for obtaining the alumina optical constants n_h and k_h. In the Bruggeman approximation, n_o and k_o may be converted into n_h and k_h through

$$0 = f_o \left(\frac{\varepsilon_c - \varepsilon_o}{\varepsilon_c + \varepsilon_o}\right) + p \left(\frac{1 - \varepsilon_o}{1 + \varepsilon_o}\right), \qquad (4)$$

where ε_c and ε_o are the dielectric constants of the alumina and the air/alumina composite membrane, respectively, f_o is the volume fraction of the alumina, and p is the porosity $(1 - f_o)$. For the alumina host medium, the refractive index n_h is found to be 1.5–1.6 and the absorption index k_h is very small and can be assumed $k_h = 0$ for avoiding complicated calculation. In addition, f_m can be obtained by[15]

$$f_m = p \left(\frac{2a}{d_o}\right), \qquad (5)$$

where p is the intrinsic porosity and $2a$ is the length of the nanowire, d_o is the optical path length. The relation of p and the nanowire radius $2b$ versus electrolyte and anodic voltage are plotted in Fig.4. The nanowire length $2a$ and the optical path length d_o can be estimated from TEM images.

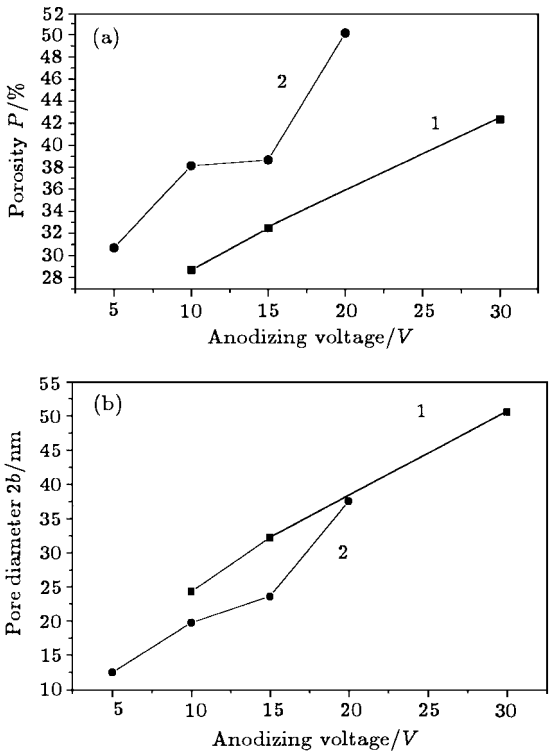


Fig.4. The variation of (a) porosity and (b) pore diameter of AAO with the applied voltage in (1) oxalic acid and (2) sulfuric acid.

In addition, when n_k, $2a$ and nanowire radius $2b$ are obtained, then k and q can be obtained using the following equation[15]

$$k = \frac{1 - q}{q}, \quad q \approx \frac{1/b}{1/a + 2/b}, \qquad (6)$$

where q is the Lorentz depolarization factor. Figure 5 shows the variations of depolarization q and k versus nanowire aspect ratio. The screening parameter k may take the values of 0, 1, 2 and ∞ for the cases of maximum screening, two-dimensional isotropic screening, three-dimensional isotropic screening, and zero screening, respectively. Screening vanishes for one-dimensional needle-like nanowires since the photon field is oriented parallel to the nanowires as the aspect ratio increases to infinity ($a/b \to \infty$).

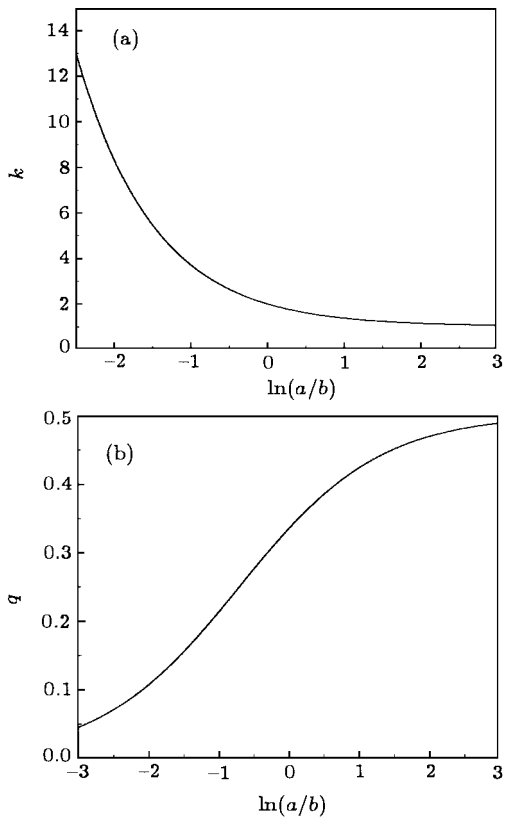


Fig.5. (a) Variation of k with the nanowire aspect ratio a/b; (b) variation of q with aspect ratio a/b.

The MG approach overestimates $\lambda_{\max}$ in all cases and most seriously at the largest particle radius (for the spherical case). Fortunately, $\lambda_{\max}$ of a higher aspect ratio in nanowire composites is almost quantitatively amenable to experimental data. In our work, a method is used to fabricate Pt nanowire arrays of small radius relative to the wavelength of light by electrodepositing into AAO templates. Indeed, it has been proven that the AAO membrane is a better host template than commercially available anodic aluminium because it can ideally control the nanowire diameter and aspect ratio. When aluminium is anodized in different acidic electrolytes, such as sulfuric acid, oxalic acid and phosphoric acid, it forms porous alumina membranes with uniformity in diameter of ordered hexagonal holes.[16] In fact, Mie scattering theory[13] is applied to particles of any size but is limited to the particles whose interparticle separation is much larger than the incident wavelength.[13] The MG theory is adapted to the particles whose dimensions are infinitely small relative to the incident wavelength.

4. Conclusions

Arrays of Pt nanowires with various diameters have been successfully prepared by electrodeposition of Pt into the pores of AAO membranes. The Pt nanowires with fcc structure are observed by XRD and TEM. The membranes ensure the electrical isolation of metal nanowires, thus maximizing the metal–insulator composite transparency at moderate volume fractions of the metal f_m. The physical origin of transparency is the development of screening depolarizing charges on the surface of small metal nanowires. By measuring UV-VIS spectra of Pt/AAO composites, we find that their optical absorption peak shifts to shorter wavelength when the nanowire diameter decreases from 90 nm to 24 nm. The simulation results based on MG theory also exhibit the blueshift. By comparison, the experimental results are qualitatively in agreement with the simulation spectra obtained using MG theory for metal–insulator composites. This phenomenon can be ascribed to the quantum size and surface effects in Pt nanowires. However, since the MG theory is strictly valid only in the limit when wire diameters and spacings between wires are infinitely small relative to the wavelength, a better coincidence has been obtained between the experimental and simulation results for the composites containing Pt nanowires with smaller diameters. In fact, we are especially interested in the investigation of the optical spectra for nanowires with even smaller diameters. We are trying to prepare nanowires with smaller diameters since the extent of transparency to the electromagnetic wave spectrum can be further improved. It is interesting to investigate the applications of such arrays of nanomaterials in electromagnetic wave screening and stealth aircraft, chemical catalyses and photoelectronic detectors.

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