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Surface Plasmon Resonances of Palladium Nanowire Arrays Prepared by Ion Track Technology

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Abstract: Palladium nanowires with varied diameters were fabricated using ion-track templates coupled with electrochemical deposition. The morphology and crystallographic structure were characterized with Scanning Electron Microscopy, Transmission Electron Microscopy, X-ray diffraction (XRD). The plasmonic responses of the as-prepared nanowires were investigated by UV-Vis-NIR spectroscopy and the simulations based on the finite-difference time-domain algorithm. The results demonstrate that the surface plasmon resonances of Pd nanowire are sensitive to the wire geometry, but also influenced by the incidence angle of light. The frequency of the transverse dipolar plasmon resonance of nanowire arrays shifts within a wide range from visible to near infrared. With increasing of wires' diameter or length, the resonance peak shifts to the red. With increasing of incident angle, a new peak appears, which is possibly assigned to the excitation of the longitudinal resonance. In addition, numerical simulations disclose that propagating surface plasmon polaritons can be excited on the palladium nanowires and the wavelength of the resonance peak is in good agreement with the experimental results.

Key words: ion track; palladium nanowires; surface plasmon resonances; UV-Vis-NIR Spectroscopy

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1 Introduction

One-dimensional nanostructured palladium materials offer exciting potential applications in diverse fields such as catalysts, nano-sensors, biomedical detections and exhibit extraordinary properties in hydrogen sensing[1–4] a3.nd hydrogen storage. In the past several years, Pd nanowires have been attracting considerable attentions due to the short diffusion length[5]. This phenomenon may differ from some other metallic nanowires (*e.g.* Au nanowire, Cu nanowire) both in their thermodynamic and phase transitions[5–6]. The property of this nanostructure is based on the surface plasmon resonance (SPR), but the SPR properties of Pd nanowires are not demonstrated yet. It is usually predicted that the SPR of Pd nanostructures, such as Pd nanowires, Pd nanoparticles, and Pd nanotubes could enhance the electric field in the vicinity of the nanostructures[7]. This may lead to superior properties than other materials, for instance, in hydrogen sensing applications. Previous studies exhibited that the LSPR of Pd alloy nanowire can be discovered and used for optical waveguides[8]. Restricted to the nanoscale dimensions and the relatively large irradiation size, the efficiency of the photon-to-plasmon conversion is much lower than the normal conditions. Only a small portion of irradiated light can be intercepted by the nanowire. Furthermore, plasmonic responses of nanowires which have experienced a constant change are received much concern. This peculiar discovery related to optical properties leads to the strong absorption and scattering in the ultraviolet, visible, and near-infrared light range. The surface enhanced spectroscopies also have a great development

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due to the highly enhanced electric field in the close vicinity of nanowires (near field). For nanowires, plasmonic properties are not only influenced by the dimensions on the nanometer scale, but also the spacing between the adjacent wires, as well as shape and size of the wire[9]. In this case, diverse SPR modes can be excited along the directions parallel and perpendicular to the long wire axis, known as longitudinal mode and transverse mode, respectively.

To date, diverse methods were proposed to fabricated Pd nanowires. Previous works have exhibited that the single-crystal Pd alloy nanowires can be synthesized via thermal evaporation method and the surface plasmon resonance was found in single Pd alloy nanowire waveguide[8]. In addition, Pd nanowires can be also fabricated by template-based strategies like electrochemical deposition in anodic aluminum oxide (AAO) templates[10–16] and chemical reaction in porous polycarbonate template[17]. Some chemical methods, such as chemical reaction[18], lithographically patterned nanowire electrodeposition (LPNE)[19], galvanic displacement deposition[20], chemical vapor infiltration[21], and electroless deposition[22] have been employed to prepare Pd nanowires as well. Taken together, concerning about utilizing various methods to fabricate Pd nanowires, there are still great challenges to realize the SPR properties.

Herein, we examine the optical properties of Pd nanowires fabricated using ion-track template coupled with electrochemical deposition. In such a case, the arrays consisting of parallel nanowires are used for several characterizations such as energy-dispersive X-ray spectroscopy and the X-ray diffraction[23]. The experimental spectra obtained from UV-Vis-NIR extinction spectroscopy are in a great agreement to the simulations based on the finite-difference time-domain algorithm. The results demonstrate that SPR properties of Pd nanowire are not only sensitive to the wire geometry, but also influenced by the incident angle of light. The frequency of the transverse dipolar plasmon resonance of nanowire arrays shifts within a wide range from visible to near infrared and can be tuned. We hope our results give some hints for promoting Pd nanowires in applications such as hydrogen sensing[24–26].

2 Experimental section

The Pd NW arrays were fabricated by ion track template-assisted electrochemical deposition. First, the polycarbonate (PC) foils (Makrofol N, Bayer Leverkusen) were irradiated by swift heavy ions at the Heavy Ion Research Facility in Lanzhou (HIRFL) with 9.5 MeV per nucleon ^{209}Bi ions at normal incidence. The thickness of templates is 30 μm and the fluence of irradiation was 1×10^{8} ions/cm^{-2}. Secondly, each surface of the irradiated polymer foils was exposed to ultraviolet light for 2 h. This procedure is usually called track sensitization and would enhance the track etching rate. The procedure is also significant for forming cylindrical nanopores in high quality. Then these membranes were etched in 5 mol/L NaOH solution at 50 ℃ to achieve cylindrical pores with diameters ranging from 45 to 235 nm which are determined by etching time. Simultaneously, an ultrasonic field was applied to achieve homogeneous etching during this process. Immediately after etching, the foils were intensively washed with deionized water in an ultrasonic field to remove residual NaOH, especially inside pores, to avoid excess etching. Thirdly, an electrochemical deposition method combined with ion-track template was conducted to prepare Pd nanowire arrays. A thin gold layer was sputtered onto one side of the template and the layer was further reinforced electrochemically by a Pd and Cu layer with a thickness of several microns. This backing layer (Au+Pd+Cu) served as the cathode during the electrochemical deposition of Pd nanowires. An aqueous solution consisted of 20 gl^{-1} K_2PdCl_4 and 20 gl^{-1} H_2SO_4 was used as electrolyte. Direct current (DC) electrochemical deposition was employed. A picoammeter (Keithley 6482) was conducted to monitor the deposition process by recording curves of deposition current versus time. The procedure would not be stopped until the wire caps reached the membrane surface, to ensure that the nanopores were entirely filled. The wire length was controlled by the deposition time. Finally, after the deposition process, the polycarbonate template was dissolved in dichloromethane (CH_2Cl_2) and then Pd nanowires were achieved.

The morphology and crystallinity of the Pd NW arrays were examined by several approaches. For the crystallographic orientations, the X-ray diffraction (XRD, PANALYTICAL X'PERT[3] POWDER) was used while nanowires were remained embedded in the templates. And scanning electron microscopy (SEM, FEI NANO-SEM 450), as well as transmission electron microscopy (TEM, FEI TECNAI G2 F20), energy dispersive X-ray spectroscopy (EDS), and selected area electron diffraction (SAED), were conducted to investigate the morphology, composition, and crystallinity of nanowires. For UV-Vis-NIR extinction spectroscopy, the wires were remained embedded in templates, while the backing layers (Au +Pd+Cu) were removed. With an UV-Vis-NIR spectrometer (PERKIN ELMER, LAMBDA 900), the extinction spectra were measured in a standard transmission geometry with respect to several parameters, such as angle, diameter, length of nanowires.

3 Results and discussion

The fabrication and characterization procedures of Pd nanowires are briefly divided into five steps (Fig. 1): irradiation with swift heavy ions, etching of latent tracks, sputtering of electrodeposition cathode, electrochemical deposition of nanowires, and characterizations with SEM, TEM, and UV-Vis-NIR Spectroscopy.

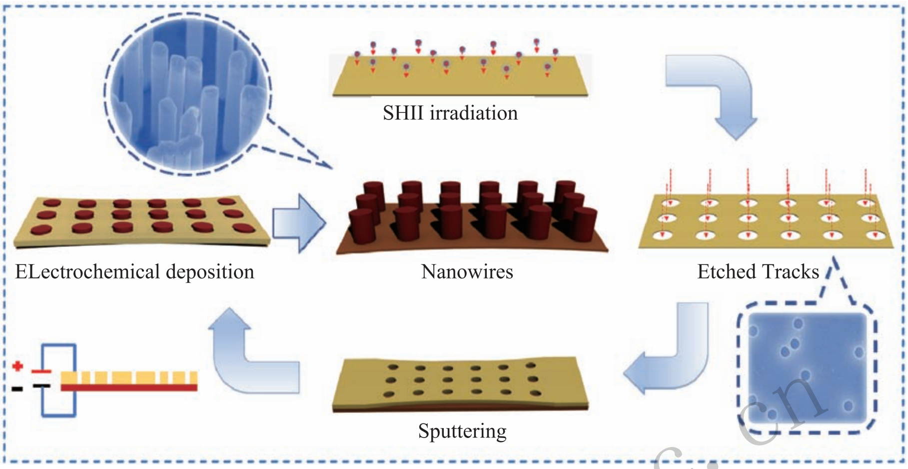

Fig. 1 (color online) Schematics of fabricating nanowires by ion track-etched templates.

The morphological and crystallographic characteristics of Pd nanowire arrays were examined by several approaches. The morphology of Pd nanowire investigated by SEM is shown in Fig. 2(a). The diameter of nanowires is approximately 140 nm, which were deposited at room temperature under applied voltage of 0.4 V. It exhibits that the vertically-standing wires are in good cylindrical shape and have smooth and homogeneous contours. The further study shows the Pd nanowire is in great crystallinity which is revealed by HRTEM [Fig. 2(b)]. In this case, the excellent crystallinity of Pd nanowires is observed within several micrometers along the wire's length. The distance between each space lattice is about 0.229 nm, which reveals the (111) lattice plane. In addition, the Pd signal is observed in the EDS spectrum [Fig. 3(a)], indicating that the nanowires are exclusively composed of Pd element. It should be mentioned that the Cu signals were from the Cu grid. The XRD spectra [Fig. 3(b)] of the nanowires exhibit multiple peaks which are assigned to the (111), (200), (220) crystalline planes, respectively.

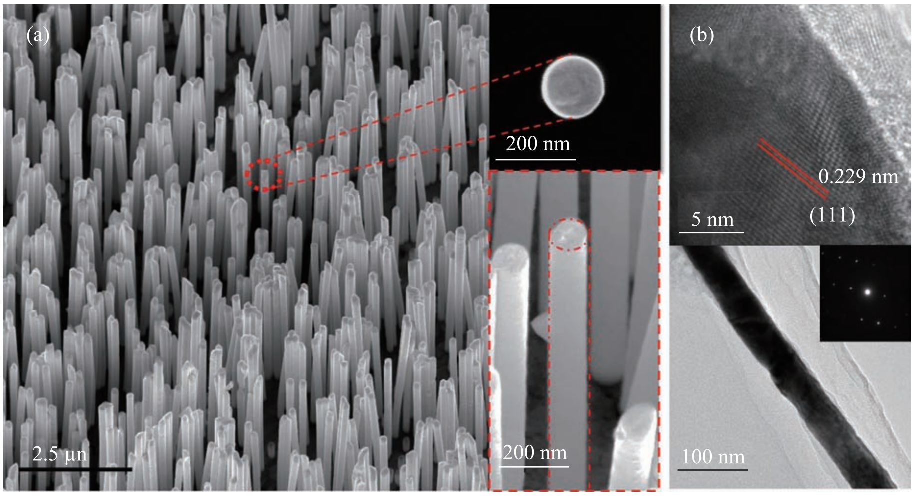

Fig. 2 (color online) (a) SEM image of Pd nanowire arrays (left) and single Pd nanowire (right). (b) Morphological analysis of single Pd nanowire by HRTEM, the inset is the corresponding SAED patterns.

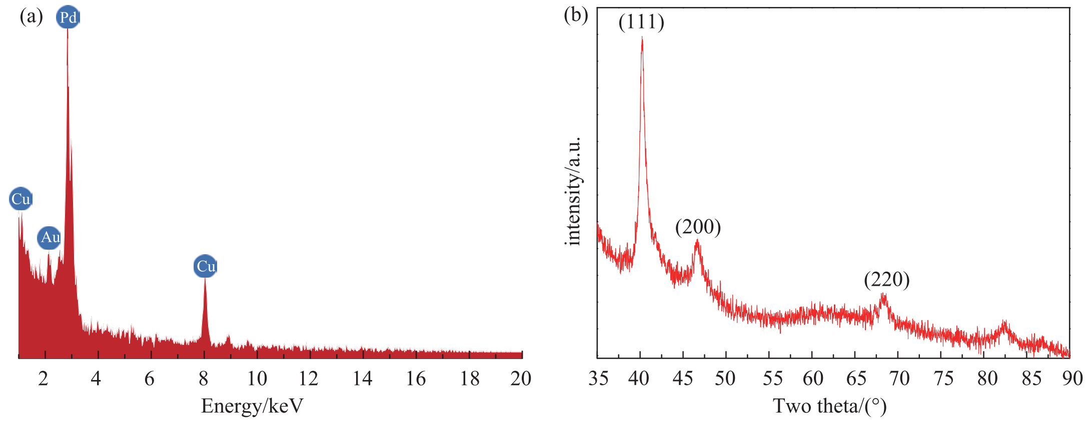

Fig. 3 (color online) (a) EDS spectrum of the as-prepared Pd nanowires; (b) the XRD spectra for the Pd nanowire arrays.

SPR properties of Pd nanowires were investigated by the UV-Vis-NIR spectroscopy and the finite-difference time-domain (FDTD) numerical simulations, as well as the Gans' theory. Concerning the shape, nanowires could be treated as nanorods in a larger aspect ratio (length over diameter). Previous works have demonstrated that the LSPR modes in randomly distributed nanorods could be varied along the directions parallel and perpendicular to the long wire axis. We denote the plasmon modes, oscillating parallel or perpendicular to the long wire axis, as longitudinal or transverse mode, respectively. Furthermore, the transverse mode of nanorods with a comparatively small diameter can be theoretically described within the framework of the Gans' theory[27], which is a quasi-static approximation method and extended from the Mie Theory:

$$\frac{\gamma}{NV}=\frac{4\pi\varepsilon_m^{\frac{3}{2}}}{3\lambda}\frac{\left(\frac{1}{P}\right)^2\varepsilon_2}{\left[\varepsilon_1+\left(\frac{1-P}{P}\right)\varepsilon_m\right]^2+\varepsilon_2^2}.$$

Here, γ is the extinction coefficient, λ is the wavelength of the incident light in vacuum, N is the number of nanorods, V relates to the volume of a single nanorod, ε_{m} is the dielectric constant of the surrounding medium, and P denotes a geometrical factor where the aspect ratio of the nanorod considered. The real and imaginary parts of the dielectric constant of Pd are represented by ε_1 and ε_2, respectively. For the calculation, the factor P is set to 0.5. The calculated spectrum shows the λ of SPR is about 730 nm, which is in excellent agreement with the experimental λ of dipolar resonance (735 nm) measured, see the extinction spectra displayed in Fig. 4(c). In addition, we also examined the electric-field distribution of a nanowire under the excitation of resonance wavelength. The results shown clearly in Fig. 4(a) evidence that a propagating SPR is excited with a propagating direction along the wire's length. In this case, the electric field at the both ends of the wire are dramatically amplified and the electric field at the bottom is significantly larger than that at the top. This hints that our palladium nanowires could serve as plasmonic platforms because such an enhanced electric field can be used to enhance several spectroscopies, such as Surface Enhanced Raman Spectroscopy (SERS).

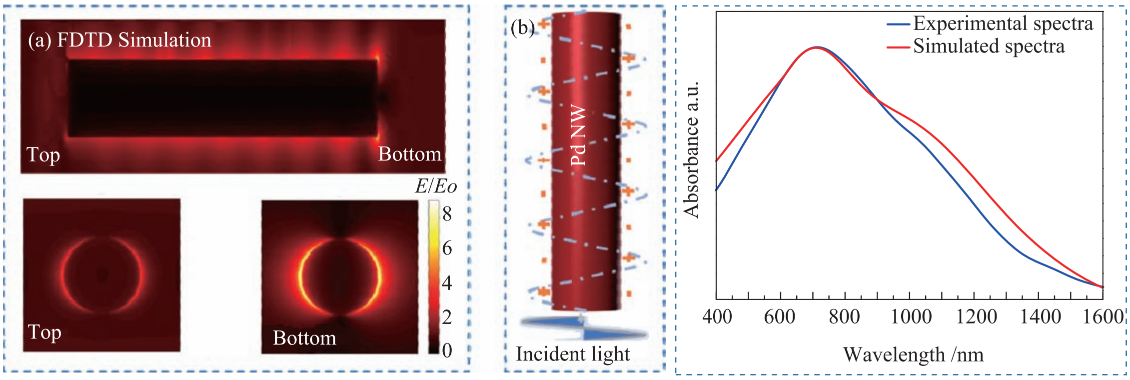

Fig. 4 (color online) (a) Simulated electric field of the single Pd nanowire which diameter is about 140 nm and has a length of 1.6 μm by FDTD algorithm. (b) The schematic diagram of surface plasmons on a single Pd nanowire. (c) The simulated and experimental extinction spectra of corresponding Pd nanowire arrays.

The UV-Vis-NIR extinction spectra of Pd nanowires in varied diameters are shown in Fig. 5(a). For these nanowires, the length is about 30 μm, and the area density of the template is about 1×10^8 wires/cm^2, assuming that the channels were basically filled. It can be seen that, with increasing diameter from 47 to 235 nm, the resonance peak dramatically shifts to the red, within a range from 735 to 1 200 nm. Because the electric field vector of incident light is perpendicular to the long wire axis, only transverse mode can be excited in this configuration. In addition, previous works have demonstrated that the electric field induced by SPR could be further enhanced when electromagnetic coupling appears between interacting metal nanostructures[28–33]. This means strong plasmonic coupling could be achieved in our Pd nanowires by increasing areal density of nanowires, in other words, irradiation fluences. To further investigate the plasmonic properties of the Pd nanowires, we checked the plasmonic responses with respect to wire length and incident angle of light. The UV-Vis-NIR extinction spectra with different lengths ranging from 0.16 μm to 2.67 μm are exhibited in Fig. 5(b). With the electric field vector perpendicularity to the long wire axis, it performs a similar trend that the dipole resonance peak shifts to the red with increasing the length of Pd nanowire. According to our previous study on Cu nanowires[9], the redshift can be attributed to on-wire coupling effect and such coupling may give rise to cumulative plasmon field enhancement. With increasing the length, the enhancement effect increases as well. Since the length of nanowire is significantly larger than the diameter, the Gans' theory is no longer valid due to the super-large aspect ratio. Previous work shows that the aspect ratio L/d can be suitable in the range $1.8< L/d <49$[27]. Thus, to investigate the origin of the extinction spectra, FDTD algorithm, which is based on the Maxwell equations, was conducted to simulate the experimental results. The corresponding extinction spectra of Pd nanowire with different length were simulated by FDTD and the results are shown in Fig. 5(c), showing a great agreement with the experimental results in Fig. 5(b). The diameter was 140 nm and the length of the nanowires were 0.16, 1.6 μm, and 2.67 μm, respectively. Taking into consideration the simulation results shown in Fig. 4(a), the collective oscillations of conduction electrons are not localized anymore and propagate along the long wire axis. This propagating surface plasmon resonance (SPP) allows that the oscillations induced by the incident light can transmit through the wire length and it has a great efficiency to enhance the intensity of electric field around the Pd nanowire structure. In these simulations, the light source was 737 nm. The schematic description of

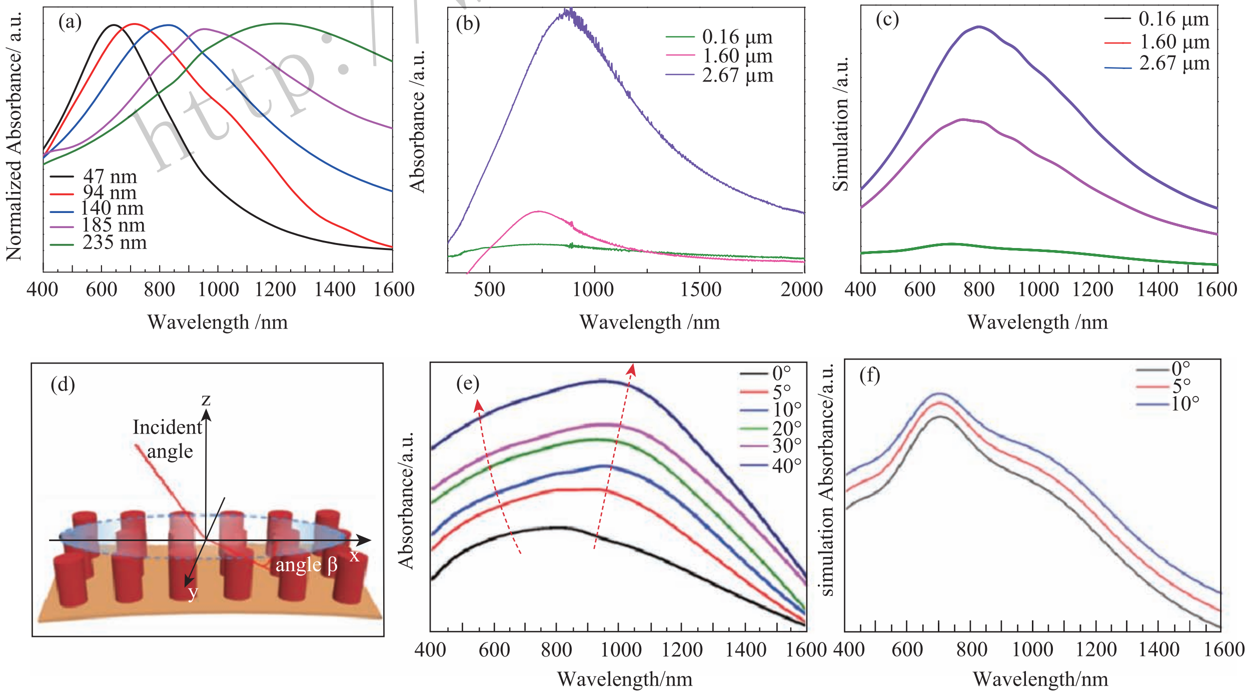

Fig. 5 (color online) (a) the UV-Vis-NIR extinction spectra of Pd nanowires in varied diameters; (b) the UV-Vis-NIR extinction spectra of Pd nanowires in different lengths; (c) corresponding simulated extinction spectra to (b); (d) Schematics of the incident angle and the angle β; (e) the UV-Vis-NIR extinction spectra with diverse incident angles; and (f) are simulated extinction spectra corresponding to (e).

counter-oscillating dipoles alone the single nanowire due to a phase shift of the incident field demonstrated in Fig. 4(b). In this case, the surface plasmon resonance (SPP) propagates from the top to the bottom of the wire.

The plasmonic responses of Pd nanowires are further studied with respect to the incident angle of light. As shown in Fig. 5(e), the UV-Vis-NIR extinction spectra exhibits that the peak position of the transverse mode is highly dependent on the incident angle of light. The corresponding extinction spectra simulated by FDTD solution are shown in Fig. 5(f). For the incident angle=0°, the transverse mode was only excited and shows a single dipolar resonance peak at ~750 nm. With increasing the incident angle, the peak gradually shifts to the blue. In addition, another resonance peak which is possibly attributed to longitudinal mode is found at 1 050 nm. When the incident angle is further increased, in contrast to transverse mode, the peak of longitudinal mode shifts to the red. In this case, the diameter and the length are about 140 and 160 nm, respectively.

To have a better understanding of SPR, further UV-Vis-NIR measurements were conducted to study the influence of incident angle on the resonances, using a polarized light source. The extinction spectra of various angles are shown in Fig. 6. The angle marked by β is defined as the angle between the polarization direction of the polarizer and the short axis (*i.e.* diameter) of the Pd nanowire. In such a case, 0° means the polarization direction of the polarizer is parallel to the short axis of the Pd nanowire. While 90° means that they are perpendicular. For the extinction spectra exhibited in Fig. 6(a), when the incident angle is 0°, the spectra exhibit single dipole resonance peak and the peak doesn't shift with increasing the angle β. The wavelength of the dipolar peak is about 730 nm. However, when increasing the incident light to 40° [Fig. 6(b)], multiple peaks appear. Based on these observations, one may conclude that more plasmonic modes are excited and the dipolar resonance shifts to the blue gradually. The peak position, as a function of the angle β, is plotted in a polar graph shown in Fig. 6(d). For the dipole peak, related to the transverse mode, with increasing the angle β from 0 to 90, the dipolar peak shifts from 925 to 960 nm.

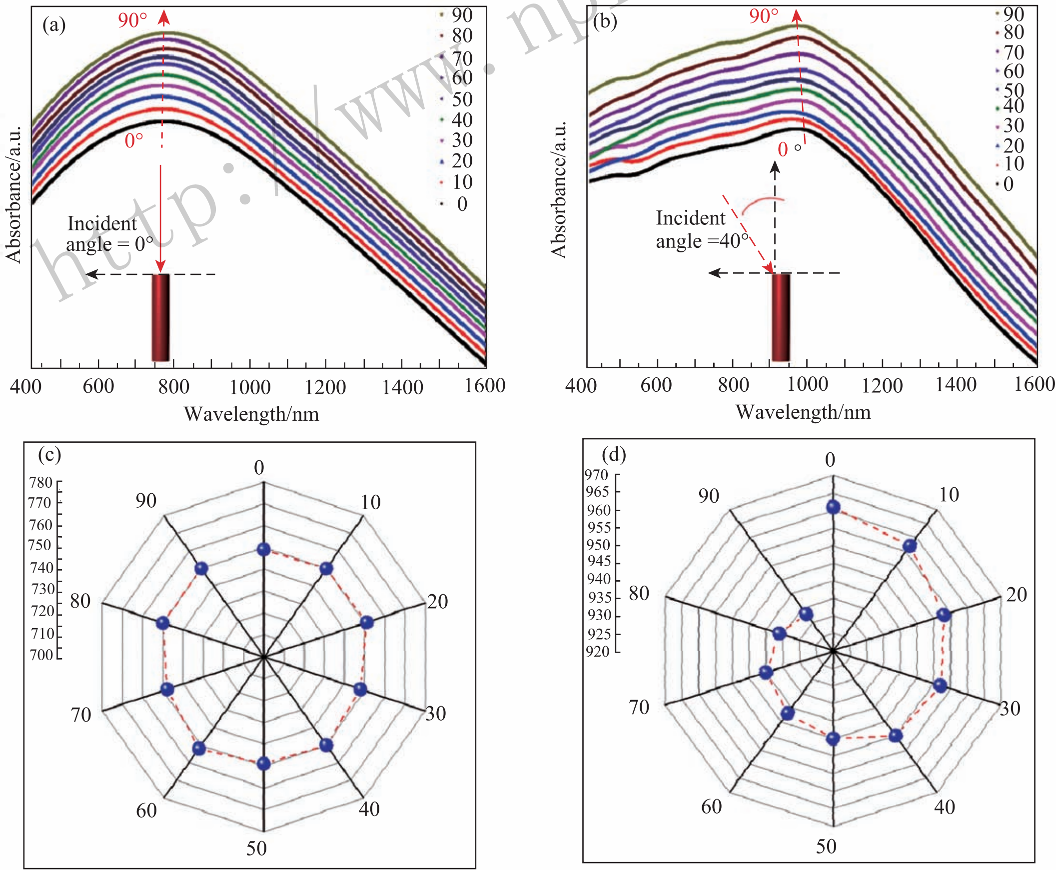

Fig. 6 (color online) The extinction spectra with polarized incident light of various angle. (a) the incident angle=0°; (b) the incident angle=40°; (c) and (d) are corresponding polar graph of (a) and (b).

4 Conclusions

In this work, Pd nanowire arrays with varied diameters and lengths were synthesized within ion track-etched templates by electrochemical deposition. The plasmonic responses of Pd nanowires were systematically studied with respect to geometrical parameters. The plasmonic modes are experimentally observed and numerically verified by finite-difference time-domain algorithm. The transverse dipolar resonance is found to be highly dependent on wire diameter, length, angle of incidence, as well as the incidence polarization.

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利用重离子径迹模版法制备出的钯纳米线阵列的表面等离激元共振现象研究

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摘要： 利用电化学沉积在重离子径迹模版中制备出了不同直径的一维钯纳米线。利用扫描电子显微镜、透射电子显微镜和X射线衍射等多种手段对制得的钯纳米线进行了形貌和结构表征。利用紫外可见光谱仪分析了钯纳米线的光学响应，发现钯纳米线存在表面等离子体共振现象。随着纳米线直径和长度的增加，其表面等离子体共振峰位发生红移；通过改变光谱测试中激发光的入射角度，其表面等离激元共振模式会随着角度的增大而变多，这可能是在横向振动模式的基础上激发了沿纳米线长度方向振动的纵向模式。与此同时，基于时域有限差分法对钯纳米线的表面等离子体共振特性进行数值模拟，结果与实验符合较好。

关键词： 离子径迹；钯纳米线；表面等离激元共振；紫外-可见-红外吸收光谱

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