

Raman and AFM Characterization of Au and Cu Nanorod and Nanowire Arrays

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Detailed abstract: Recently metal nanowires (nanorods) have aroused tremendous interest because of their novel properties and potential applications in wide fields^[1]. Many two-dimensional nanowire arrays of semiconductors and metals with different diameter and length have been made by using template synthesis method. To characterize the novel optical, electronic and magnetic properties of these materials, UV-Vis and fluorescence spectroscopies are two of the most widely used methods^[2, 3]. Raman spectroscopy has, however, only been applied to the characterizing of semiconductor nanowires and carbon nanotubes^[4, 5]. Important and meaningful information can be obtained in these cases, as some forbidden Raman modes in the bulk materials become Raman active^[4, 5]. Raman spectroscopy is apparently not suitable to study metal nanowires since it can only detect the mechanical vibration bands located in the extremely low frequency region. Consequently, an alternative way has to be established to study the metal nano-wires (-rods) with Raman spectroscopy.

In the present work, we have taken the probe molecule strategy and used surface-enhanced Raman spectroscopy (SERS) to characterize metal nanorods (nanowires). It is well known that for a molecule which interacts strongly with a surface, its vibrational band frequency and shape are very sensitive to the electronic property, the chemical environment and the morphology of the surface. Hence Raman spectroscopy has long been used to analyze the atomic structures and the electronic properties of the surface indirectly through assessing carefully the spectral changes of

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the adsorbate known as a probe molecule. On that account, it is of great interest to diagnose the electronic structures of the metal nanorods with the vibrational spectrum of a probe molecule. We have examined the changes in the electronic properties of the nanorods through analyzing the spectral changes of the probe molecule. For this purpose a typical SERS molecule of SCN^- was employed.

The nanorod arrays of Au and Cu with different diameter from about 15 nm to 130 nm were fabricated electrochemically by means of the anodic aluminum oxide (AAO) templates. To partially expose metal nanowires with various lengths, the AAO template was chemically etched off to a certain extent by an aqueous solution of phosphoric acid or sodium hydroxide as shown in Fig. 1. After the template was etched off, the nanowires can be characterized by TEM, see Fig. 2. The tapping mode AFM image was obtained on a scanning probe microscope (Nanoscope IIIa). SERS measurements were performed on a confocal microprobe Raman system (LabRam D).

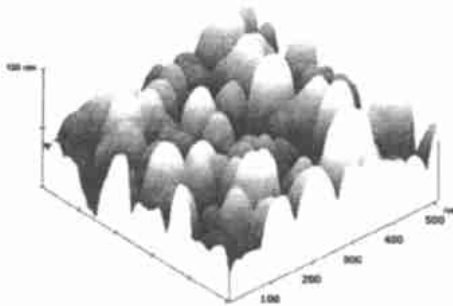


Fig. 1 AFM image of the Cu nanowire at the initial stage of the dissolution process to remove the AAO template



Fig. 2 TEM image of the single Au nanowire after completely removing of the AAO template

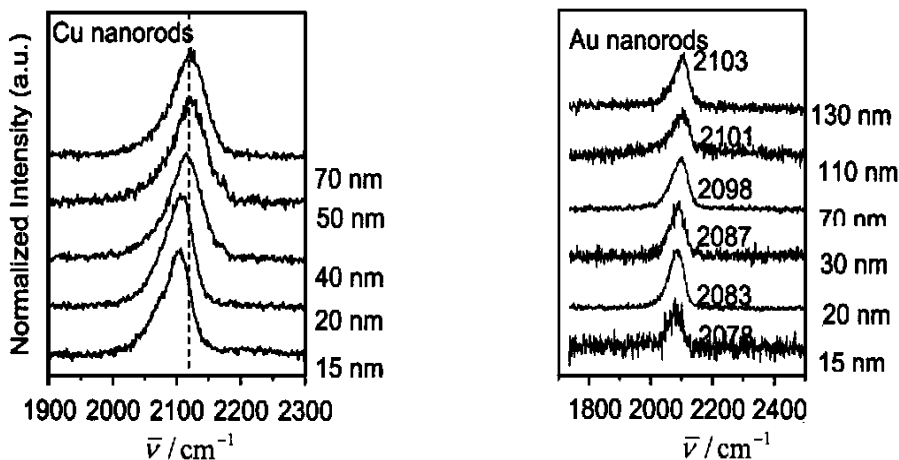


Fig. 3 In situ SERS spectra of SCN^- adsorbed at the Cu and Au nanowires with different diameters. The solution was 0.01 mol/L NaSCN and 4% H_3PO_4

It is of special interest that the vibrational frequency of the probe molecules adsorbed at metal nanorods critically depends on the diameter as shown in Fig. 3. . The effect on the frequency by the nanorods' diameter varying in several tens of nanometers is equal to that by the applied potential of about several hundred millivolts in the electrochemical system. This frequency-diameter dependence could be mainly contributed by the change of the electronic structure (Fermi level) of nanorods with different diameter.

It is well known that only when the metal particle becomes as small as 1 ~ 2 nm, the quantum-confinement effect can be observed. In our case, the smallest diameter of the nanorods is about 15 nm as shown in the TEM image (Fig. 2). Therefore it seems that other effects on the Fermi level and the surface effect and small size effect may play an important role. If a bulk metal is cut into small size with scale that is about the scale of the electron mean free path (about 50 ~ 100 nm for Cu metal), many physical properties of these nanoparticles (nanorods) will be changed remarkably. The good agreement has been made in our theoretical calculation on the Fermi energy that will change dramatically when the diameter of nanorod decreases from 70 nm to 10 nm. It has been shown that by applying the probe molecule strategy, surface Raman spectroscopy could be developed as a new diagnostic tool for metal nanorods (nanowires).

Key words: Anodic aluminum oxide template, Nanowires, Surface-enhanced Raman spectroscopy, Thiocyanide

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金、铜金属纳米棒或纳米线的 AFM 和 SERS 的研究

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摘要: 通过电化学氧化法制备具有不同孔径氧化铝模板,利用交流电镀的方法在模板中沉积金属,再用酸溶解模板可以得到相应尺度的金属纳米线或纳米棒的阵列.本文利用原子力显微镜和表面增强拉曼技术分别表征了金和铜两种金属纳米线阵列.研究表明,作为探针分子的硫氰(SCN^-)在金属纳米线上的碳氮三键的振动频率随纳米线直径的增大而蓝移.这一现象可能是因为尺寸效应对纳米线的费米能级造成影响,使不同直径的金属纳米线电子结构存在微小的差别.

关键词: 氧化铝模板;纳米线;表面增强拉曼光谱;硫氰