Surface enhanced Raman scattering from transition metal nano-wire array and the theoretical consideration

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Abstract

Co, Ni, Pt and Pd nano-wire arrays with diameter of about 50 nm were fabricated by means of template synthesis. By alternating current (AC) electrodeposition these metals were filled into channels of anodic aluminum oxide (AAO) film respectively. Nano-electrode arrays having good electric contact with the substrate was also fabricated by employing combined electroless deposition and the AC electrodeposition. Strong surface enhanced Raman scattering (SERS) was observed from both metal nano-wire arrays and nano-electrode arrays after partial removal of the AAO film. The SERS intensity of probe molecules adsorbed at the arrays depends critically on the length of the nano-wire explored at the surface. The experimental results agree well with the corresponding theoretic calculations based on electromagnetic enhancement. The lightning rod effect may play an important role for the enhancement of the Ni nano-rod under the favorable length. It has been shown that metal nano-wire arrays can be developed to a new generation of substrate exhibiting very high SERS activity, especially for transition metals. These well-ordered surface nano-structures can also be served as a proper model for the SERS mechanism study.

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1. Introduction

In mid-1970s, it was discovered largely through the work of Fleischmann, Van Duyne, Creighton, and their co-workers that molecules adsorbed on electrochemically roughened silver surfaces produce a Raman spectrum that was at times a millionfold intenser than what was expected [1–3]. Since then, there have been thousands of papers dealing with this abnormal phenomenon dubbed surface enhanced Raman scattering (SERS), either theoretically or experimentally [4–9]. Various experimental characteristics of SERS have been revealed [10–13]. For example, the effective increases in the Raman scattering cross sections, or surface enhancement factors (SEF), with about typically 10^6-fold are obtained only on roughened silver, gold and copper substrates. Recently, we have reported that good-quality surface Raman spectra

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can be obtained from transition metals with the development of several surface roughening procedures [14–16]. Many transition metals exhibit relatively weak surface enhancements and their SEF values depend on the nature of the metal and surface pretreatment, e.g. $10^3$–$10^4$ for Pt, Rh, Ni, Co and Fe, and $10^1$ for Pd [16–20].

It has been found that surface preparation is crucial to produce SERS signals for both noble and transition metals [1–4,9–12,16–18]. A variety of surface morphologies are employed in SERS studies, including surfaces roughened by one or more oxidation–reduction cycles (ORC), surfaces roughened by chemical etching in acids, island films deposited on surfaces at elevated temperatures, rough films deposited by evaporation or sputtering in vacuum onto cold (100 K) substrates or by electrochemical deposition, colloids (generally aggregated colloids) generated by chemical method or laser ablation. These surfaces in general have a very broad distribution of roughness feature from micron to atomic scale. This drawback has caused some confusions and arguments on issues such as which portion (or scale) of surface roughness plays a key role in optimizing the SERS activity. Moreover, the randomly rough surface is most unfavorable in theoretic modeling of the SERS mechanisms.

Recently enormous enhancements with the SEF up to $10^{14}$ have been reported [21–24]. The high-quality SERS or surface-enhanced resonance Raman scattering (SERRS) spectra from a single molecule adsorbed on silver nano-particles can be obtained. More interestingly, only the nano-particles with the size of 80–100 nm are responsible for the optimum value [22]. It clearly reveals that the new generation of SERS substrate exhibiting the highest activity must have a very narrow distribution of roughness feature in particle size and shape. Thus, the well-ordered surface nano-structure is highly desirable for both fundamental and applied studies.

In fact several approaches to prepare highly ordered periodic arrays of nano-particles have been made since 1980s. The first one was reported by Liao et al. in early 1980s [25]. They obtained regularly ordered SERS substrates by depositing Ag particles over periodic arrays of silica posts that were fabricated by the IC lithography. Due to the limitation of spatial resolution for the lithography at that time, the particle size was as large as about several hundred nano-meters, which is not a proper size according to the SERS theory [4,5]. Such type of SERS substrate has been further developed by nano-sphere lithography [26,27], in which SERS active metal is evaporated into preformed arrays of nano-pores which are then removed, leaving behind the metal particles formed in the interstices.

A novel procedure has been developed by Natan et al. based upon the self-assemble monolayers technique in mid-1990s [28]. It can regularly arrange monodispersed colloid gold and silver particles onto functionalized metal or glass substrates, producing SERS substrates with good reproducibility and stability. The advantage of the method is the ease of control of particle size and density, and the space between the substrate and the particle. Thus one is able to tune the electromagnetic (EM) characteristics of the surface, which would be helpful for systematic study of the SERS mechanism.

It should be pointed out that the SERS activity depends not only on the particle size, but also the particle shape. Many theoretic studies based on the EM enhancement have predicted that SERS intensity will increase significantly with increase of aspect ratio of the nano-particles. On the other hand, the two-dimensional nano- or micro-particle arrays mentioned above do not have electric contact with the substrate. Tuning of the electronic property such as Fermi level is not feasible for those systems. Therefore, it is necessary to seek other approaches capable of well controlling both the diameter and aspect ratio of nano-rod arrays in order to surmount the above-mentioned problems.

Recently, template synthesis method has attracted extensive interest in nano-physics, -chemistry and -materials, with which, variety of nano-materials of novel properties and wide-ranging potential applications have been produced [29–32]. Many two-dimensional nano-wire arrays of semiconductors and metals, with different diameter and length have been fabricated by this method [29–35]. Among these template synthesis methods, the anodic aluminum oxide (AAO) seems
to be an optimize one for fabricating metal nano-wire (nano-rod) arrays [34–38]. The first stage of this approach was to prepare metal nano-wire arrays as SERS substrates. In 1995 Joo and Suh published a paper in a Korea journal on SERS of Ag nano-wire arrays [39]. Ag nano-wires were electrochemically deposited into the nano-pores of AAO films followed by partial removal of the oxide layer to give rise to a SERS signal. The result obtained did not attracted much attention as the SERS intensity obtained was weaker than that from normally prepared Ag colloids. So the authors did not continue their work along this avenue. More than four years after, our group has demonstrated that with careful preparation of AAO film, the noble metal nano-wire arrays can exhibit strong SERS activity [40].

Since the SERS activity also depends decisively on the nature of metals, such as the dielectric constant [1–4,13], it is essential to carry out systematic studies and to extend the study onto other metals, in particular transition metals that are of both fundamental and practical importance. This idea is based on the recent progress made in our laboratory that many bare transition metals exhibit weak SERS activity [13–20]. If the SERS activity of transition metals can be optimized by using nano-wire arrays, it may greatly renew interest in SERS field in the mechanism investigation and opening up many new applications. Accordingly, our present work focuses on a complementary study that is divided into two parts: (i) preparation of the metal nano-rod arrays as the substrate with high SERS activity, and (ii) development of the nano-rod arrays to become a proper model system for SERS mechanism studies.

In the present work, Co, Ni, Pt and Pd nano-wire arrays and nano-electrode arrays were fabricated by using the template synthesis method. The surface Raman spectra of pyridine adsorbed at their surface were obtained and the SERS mechanism has been studied by probing SERS effect from the Ni nano-wire arrays with different aspect ratio.

2. Experimental

In the present work the metal nano-wire arrays of Ni, Co, Pt, Pd and Cu were fabricated by means of the AAO templates which was prepared as described in Ref. [41]. By controlling the voltage applied during the formation of AAO and/or metal deposition processes, one can obtain nano-rod or nano-wire arrays with different diameters. The detailed procedures for preparing the nano-rod arrays and nano-electrode arrays will be given in the first part of Section 3. Raman spectra were acquired using a confocal micro-probe Raman system (LabRam I). The exciting wavelength was 632.8 nm from an internal He–Ne laser with a power of 12 mW on the sample surface. The detailed description on the Raman measurement has been given elsewhere [13,15]. For the in situ SERS measurements on the nano-electrode arrays, a Pt ring served as the counter electrode, and the saturated calomel electrode (SCE) was used as reference electrode. All the chemicals were of analytical reagents and solutions were made using Milli-Q water (Millipore Inc.).

3. Results and discussion

3.1. Preparation for the metal nano-wire arrays

Fig. 1 shows a schematic diagram of the fabrication procedures for metal nano-wire arrays. First, the aluminum substrate was electrochemi-

![Fig. 1. The schematic diagram of the fabrication processes of metal nano-wire arrays. (a) Formation of AAO film; (b) AC deposition of metal; (c) partially dissolution of AAO layer; (d) collapse of the metal nano-wires.](image)
cally polished then oxidized in phosphoric or oxalic solution. A two-dimensional array of cylindrical nano-pores was obtained. The diameter of the pores may be adjusted by varying the anodic voltage, the media and the temperature during the formation of the AAO film. The parallel alignment of the AAO film ensures the formation of metal nano-wires. Alternating current (AC) deposition ~50 Hz was applied to deposit the metal into the pores (as shown in Fig. 1) with voltage control from 2 to 20 V depending on the thickness of the barrier layer of the AAO film. Well-ordered metal nano-wires with appropriate length were exposed from the surface after the controlled etching of the surrounding alumina in a dilute phosphoric acid. Fig. 2 shows an AFM image of Ni nano-wire arrays after the partial removal of alumina. It can be seen that two-dimensional Ni nano-wires were parallel to each other and normal to the surface.

It should be pointed out that the metal nano-wires fabricated by the above method are separated from each other by the insulating alumina walls and so as the bottom of the nano-wires. As a consequence, the electrode potential control cannot be achieved. This limits the potential application of the nano-wires in electrochemistry. In order to overcome this problem, a variation of metal deposition was made as described in detail as follows (see also Fig. 3): Firstly, a sensitizer (typically saturated SnCl₂ ethanol solution) was applied to the template for about 10 min. During this process, the sensitizer bound to the surface via complexation with surface hydroxy groups or other groups depending on the type of the sensitizer. This sensitized AAO template was then activated by exposure to Pd²⁺ in a solution of 2 g/l PdCl₂ and 2 ml/l HCl (37%) for 3–4 min, resulting in the formation of discrete Pd nano-particles on the nano-pores and surfaces of the AAO film. After that, the Pd-coated template is immersed into a Ni or Co plating bath containing the corresponding reducing agent (typically NaH₂PO₂) for electroless deposition. The electroless deposition should proceed in a slow rate at room temperature in order for the metal to completely fill the nano-pores and protrude out to the surface (see Fig. 3). In order to make a good electrical contact for electrochemical uses, the filled template was further immersed into different Ni²⁺ or Co²⁺ containing solutions to electrochemically deposit a thick and intensive metal layers. Finally, the AAO template was turned over and the Al substrate was removed completely in saturated HgCl₂ solution. And the template was then immersed in 10 wt.% H₃PO₄ solution to removed the bottom part of the

![Fig. 2. The AFM image of Ni nano-rod arrays after the AAO layer was partially removed in solution of 4% H₃PO₄.](image)

![Fig. 3. The schematic diagram of the fabrication processes of electrical conductive metal nano-rod arrays. (a) Formation of AAO film; (b) AC electrodeposition and electroless deposition of metal; (c) turn over the substrate and dissolution of barrier layer; (d) partially dissolution of AAO layer.](image)
template (the barrier layer) followed by partial removal of the alumina walls in dilute phosphoric acid solution to obtain the upstanding metal nano-electrode arrays (Fig. 3d).

### 3.2. SERS from transition metal nano-wire arrays and nano-electrode arrays

Fig. 4 presents the good-quality SERS spectra of pyridine adsorbed at Pt, Co, Ni and Pd nano-wire arrays fabricated by AC deposition with the diameter of about 50 nm respectively. Based on the SEF calculation developed in our laboratory, the nano-wire arrays with proper lengths (vide infra) exhibit an enhancement of more than three orders for Co and Ni nano-wire arrays, and about two orders for Pt and Pd metals. The SERS signals observed are considerably stronger than or close to that from the conventionally roughened transition metal electrode surfaces in our laboratory in the past five years. It is worth noting that the SERS spectral features, including the frequency and relative band intensity, from the nano-wires are nearly identical to that of the normal bulk electrodes at the open circuit potentials. Comparing the spectral features from the four metals, one could find that the relative intensities of the SERS bands were dependent on various metals. Three bands at about 1010, 1210 and 1590 cm$^{-1}$ which could be assigned to the ring breathing, in-plane C–H deformation and ring stretching vibration were detected on the Co, Ni and Pd nano-rod arrays respectively, while only one band of the breathing vibration was observed from Pt nano-wire arrays. It was also found that the intensities of the above three bands from Co and Ni nano-wire arrays were almost identical. For the Pd nano-wire arrays, the intensities of the later two bands were about a quarter of the intensity of the ring breathing vibration mode. The differences in the relative intensities for various metal nano-wire arrays revealed that the pyridine adsorbed on the nano-wire arrays with different orientation. Pyridine adsorbed in a tilted configuration on the Ni, Co and Pd nano-wire arrays while vertical on Pt at the open circuit potential. It was also found that the intensities of the above three bands from Co and Ni nano-wire arrays were almost identical. For the Pd nano-wire arrays, the intensities of the later two bands were about a quarter of the intensity of the ring breathing vibration mode. According to the above experiment has shown that the two-dimensional nano-wire arrays are a kind of highly active SERS substrates, especially for transition metals.

Although the good-quality surface Raman spectra of pyridine adsorbed on the above four transition metal nano-wire arrays have been obtained successfully, it is still not possible to make the in situ measurements on these nano-wire arrays as they are isolated by the alumina. Nano-electrode arrays (described in Fig. 3) were, therefore, employed in the following set of experiments. Fig. 5 shows a set of potential-dependent surface Raman spectra of pyridine adsorbed on the Co and Ni nano-wire arrays respectively. The potential-dependent spectra were recorded stepwise from the negative limit to more positive potentials in order to avoid the oxidation of the reactive metal nano-wires. It can be seen that the SERS intensities change significantly with the applied potentials. This could serve as an evidence that the metal nano-wires are indeed conductive. The intensities reached their maximum value of about 15 cps at $-1.1$ V for Co nano-rod and $-1.0$ V for Ni nano-rod, respectively. The relative intensities in the above potential are similar to that from their nano-wires arrays fabricated by the first way. Moreover.

![Fig. 4. Surface enhanced spectra of pyridine adsorbed on different metal nano-wire (rod) arrays in a solution of 0.01 M Py and 0.1 M KCl.](image-url)
the spectral features from these nano-electrode arrays are almost identical to that obtained on the normal bulk electrode surfaces of themselves that were properly roughened by electrochemical ORC [13–15].

We monitored the distinctive change in SERS intensity when the alumina layer was gradually etched in sodium hydroxide solution. Fig. 6 shows that the intensity depends critically on the Ni nano-wires' length standing at the substrate surface, which was controlled by the etching time. It also presents the integrated intensity-etching time profile of pyridine adsorbed on Ni nano-wires. The SERS intensity increased quickly at the beginning and decreased suddenly after the etching time was longer than 100 s. At last, the intensity of Raman signal decreased substantially and even cannot be detected, at which the nano-wires aggregated and lay down randomly. The maximum intensity is about 20 times as strong as that of in the initial stages of the etching process. There is no doubt that the increase in intensity is partially due to the increase of the surface concentration of the adsorbate when the longer rods were exposed to the solution. However, it cannot explain the significant quenched in SERS intensity in the final etching process when the exposed surface area of nano-wires might increase to the maximum.

Fig. 5. Potential-dependent surface Raman spectra of pyridine adsorbed on the metal nano-rod arrays: (a) cobalt and (b) nickel nano-rod. The solution was 0.01 M pyridine + 0.1 M KCl.

Fig. 6. Surface Raman spectra of pyridine adsorbed on nickel nano-rod arrays when the alumina oxide layer was dissolved layer by layer in NaOH after 0 s (a), 60 s (b), 75 s (c), 90 s (d), 100 s (e) and 110 s (f). The inset was the intensity-etching time profile.
Nevertheless, the above phenomena indicate that the metal nano-wire arrays with proper length could serve as SERS substrates with high SERS activity, especially for transition metals.

3.3. A theoretical consideration of the SERS mechanism

After confirming the ordered nano-wire arrays to be good SERS active substrates, one may naturally raise a question: what we can study the SERS by taking the advantage of the nano-wire arrays in which its length and diameter can be well controlled in a certain range. The most straightforward one is to investigate the SERS mechanism. The optical property of metal nano-wire arrays depends strongly on particle size, shape and orientation when exposed to an EM field created by the incident light. Martin et al. reported the shifts in the absorption maximum and changes in the absorption intensity of the Au nano-rod arrays/AAO composites as a function of nano-wire’s diameter and aspect ratio [33,42]. Normally, the surface plasma (SP) can induce giant surface electric field for the SERS effect. It is related to the absorption band, i.e. the large EM enhancements associated with SERS are dependent on the above-mentioned feature. They hence expected that the nano-rod with a favorable shape and size would be good SERS substrates [42]. Therefore, it is essential to study the SERS effect of the metal nano-rod with different aspect ratio or diameter, which will drive the investigation on the complicated SERS mechanism(s). In this work, the Ni nano-rod arrays fabricated by AC deposition was used as the substrate because of its relatively high SERS activity among transition metals [16–18].

From Fig. 6, one can see the sudden drop in SERS intensity in the final etching stage. This intensity-etching time dependence is very hard to be explained in terms of the charge transfer (CT) mechanism [6–10] because the number of CT active sites is proportional to the surface area. Furthermore, the CT mechanism is associated with the chemical interaction between the probe molecules and the substrate surfaces. This interaction would not change with the aspect ratio of the nano-rod. Therefore, the major contribution to the dependence of intensity on the etching time is most likely due to the EM enhancement [5,43].

Based on the classical theoretical calculation for the EM mechanism [43], we used a two-dimensional array of separated prolate hemispheroids standing at the surface as the Ni nano-rod array. To simplify the calculation, the prolate–prolate interactions were not taken into account. The result obtained on the enhancement for a metal prolate hemispheroid model reveals that the enhancement ($G_M$) is associated with the aspect ratio and the wavelength of the exciting line (see Fig. 7). The enhancement increases with the aspect ratio (i.e. the length to the radius of the cylinder nano-rod) and with the excitation wavelength red shifted. It should be noted that the enhancement curve does not show the maximum in a wide range of the excitation wavelength. This is different dramatically from the noble metals of Ag, Au and Cu, and the maximum is served as the direct and strong evidence of the SP resonance in which the surface electric field was enhanced dramatically. This dif-

![Fig. 7. Enhancement of the ring breath stretching vibration of pyridine–wavelength of the laser profile of the Ni nano-prolate with the short axe of 50 nm for various aspect ratios from 1 to 8.](image-url)
ference is quite reasonable because the dielectric constant of the Ni is not proper for exciting SP resonance in the visible region. [44] Accordingly, one can conclude that the SP resonance does not play an important role in the EM enhancement for the Ni nano-rod (nano-wire) arrays.

It is necessary to emphasize that surface plasmon resonance is not the only source of enhanced local EM fields. It is well known that lightning rod effect can result in a largest electric field near the sharpest surface of the needle-like rod. As a consequence, the maximum enhancement reaches at the spheroid tip, at which the electric field is largest. The field strength also increases with the aspect ratio. [43,45] Therefore, one may assume that the lightning rod effect may play an important role for the enhancement of the Ni nano-rod under the favorable length. For the investigation of SERS from transition metals, this effect needs to be considered for a complete understanding of SERS mechanisms.

The experimental data give the SEF value of the Ni nano-wire array to be three- to four-folders enhancement in the favorable length at the excitation line of 632.8 nm. However, the theoretical calculation results show that the maximum enhancement is about $10^3$–$10^6$ for a nano-wire with aspect ratio of 8:1 at the present excitation line. Since in the actual experimental condition, there are various possible features deviated the optimize condition of classical theoretical calculation, for example, all molecules will not be located at the tip of the metal particles but will be distributed over the metal surface. It results that the actual EM enhancement is an average over the aspect ratio of the particle distribution.

Based on the above calculated results, the larger of the aspect ratio is, the higher enhancement. However, it was quite difficult to obtain the nano-wire with aspect ratio more than four experimentally as the nano-wire is easy to be collapsed on the surface. In the initial stage of the dissolution of the alumina template, the length of the emerged metal nano-rods was rather short which was observed by the AFM image. With the increase of the length of Ni nano-wire standing up at the surface, the aspect ratio became larger, thus to tune the EM characteristics of the surface. As a consequence, the intensity of the adsorbed molecule increased remarkably with the etching time, especially using the excitation line of 633 nm in the present study. It should be point out that it is impossible for the nano-rods to support themselves on the surface when they became longer and longer at the end of the dissolution process. As the result, they collapsed at the alumina surface and the surface structure changed totally. Therefore, the prolate spheroid model is not suitable for simulate such kind of highly rough surface.

In summary, both experimental and theoretical results show that the maximum enhancement can be achieved by carefully changing the aspect ratio of the nano-wire. It may provide a good reason for us to be optimistic that the template synthesis will be an advantageous tool to fabricate the new SERS active substrates, especially for the transition metals. The systemic investigation on the dependence of SERS intensity the aspect ratio of the nano-rod will be beneficial to get well-controlled SERS substrates and to get a deeper insight into the SERS mechanism.

Acknowledgements

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