

Electronic properties of metal nanorods probed by surface-enhanced Raman spectroscopy

Jian-Lin Yao,^a Xin Xu,^a De-Yin Wu,^a Yong Xie,^a Bin Ren,^a Zhong-Qun Tian*^a Gu-Ping Pan,^b Dong-Mei Sun^b and Kuan-Hong Xue*^b

^a State Key Laboratory for Physical Chemistry of Solid Surfaces and Institute of Physical Chemistry, Xiamen University, Xiamen 361005, China. E-mail: zqtian@xmu.edu.cn

^b Department of Chemistry, Nanjing Normal University, Nanjing 210097, China

Received (in Cambridge, UK) 5th April 2000, Accepted 21st July 2000

Published on the Web 9th August 2000

Applying the probe molecule strategy, surface-enhanced Raman spectroscopy has been used, for the first time, as a diagnostic tool of the electronic properties of metal nanorods; the vibrational frequency of the probe molecule SCN⁻ at Cu nanorods is shown to critically depend on the nanorod's diameter in the range from 50 to 15 nm; the upshifting of the Fermi level with a decrease of the nanorod's diameter is interpreted based on the change of cohesive energy owing to the high ratio of surface to bulk atoms.

Metal nano-rods (-wires) have aroused tremendous interest recently because of their novel properties and potential applications in a wide variety of fields.^{1–5} So far many techniques have been employed to characterize the novel optical, electronic and magnetic properties of such materials.^{2–5} UV–VIS absorption and fluorescence spectroscopies are two of the most widely used methods.^{3–5} Raman spectroscopy has, however, only been applied to characterize semiconductor nanowires and carbon nanotubes.^{6–9} Important and meaningful information can be obtained in these cases, as some forbidden Raman modes in the bulk materials become Raman active.^{6,7} Raman spectroscopic study on metal nanowires can only detect the mechanical vibration bands (also denoted inelastic Mie scattering or acoustic modes) located in the extremely low frequency region (typically 2–10 cm⁻¹).¹⁰ Consequently, an alternative way has to be established to study metal nano-wires (-rods) with Raman spectroscopy.

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 surfaces indirectly through assessing carefully the spectral changes of the adsorbate, the so called probe molecule.¹¹ On that account, it is of great interest to diagnose the electronic structures of metal nanorods *via* the vibrational spectrum of a probe molecule. In the present work, surface-enhanced Raman spectroscopy (SERS) has been used because of its extremely high sensitivity in characterizing the surface species on metals. In order to examine the changes in the electronic properties of nanorods by analysis of the spectral changes of the probe molecule, a typical SERS system of SCN⁻/Cu was employed in the present study. SERS measurements were performed on a confocal microprobe Raman system (LabRam I).¹²

The arrays of Cu nanorods were fabricated using anodic aluminum oxide (AAO) templates as described in ref. 13. By controlling the electrochemical conditions during AAO formation and/or metal deposition processes, one can prepare nanorod arrays with different diameters from *ca.* 15 to 70 nm. As the SERS intensity depends critically on the nanorods' length exposed at the surface,¹⁴ the length was varied between several tens to several thousands of nanometers, which was controlled by chemically etching off the AAO template to the desired extent in an aqueous solution of phosphoric acid or sodium

hydroxide. SERS intensities from these ordered nanorod arrays are higher than those from the electrochemically or chemically roughened electrodes even with the best surface preparation.¹⁴

Fig. 1 shows the wavenumber–diameter profile of SCN⁻ adsorbed at Cu nanorod arrays with lengths of *ca.* 100 nm but with variation of the diameter from 15 to 70 nm. The vibrational frequency of ν_{CN} is shown to critically depend on the nanorods' diameter when the diameter is <50 nm. It is essential to compare this interesting vibrational property to that of a normal Cu electrode in the same solution. The wavenumber–potential profile of SCN⁻ adsorbed at an electrochemically roughened Cu electrode is also displayed in Fig. 1. The wavenumber shows a linear downshift as the applied electrode potential is made more negative, showing a similar trend to the size effect of decreasing the diameters of the metal nanorods. It can be seen that the effect on the wavenumber upon changing the diameter from 50 to 15 nm is equivalent to that of decreasing the applied potential by *ca.* 200 mV. Similar results have also been obtained from Au and Ag nanorods. Therefore, it is of importance to reveal the reason for the wavenumber–size dependence of the metal nanorods.

The Fermi energy level is well known as one of the most important parameters, with which to characterize a metal. The Fermi level determines many of the gross electronic properties that could consequently influence the intermolecular bonding and the relevant vibrational frequency of an adsorbate. The more negative the applied electrode potential, the more upshifted the Fermi level, and so the greater tendency to supply electrons from the electrode to the adsorbate. This leads to a down-shift of ν_{CN} as found for SCN⁻/Ag.¹⁵ It is well known that if a bulk metal is cut into very small pieces whose characteristic size is about or smaller than the electron mean free path, many physical properties will be changed substantially.^{1,2} At present, we think the surface effect and small

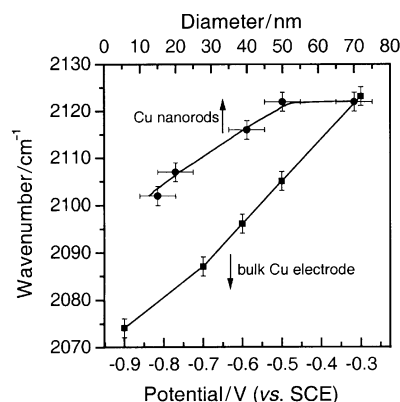


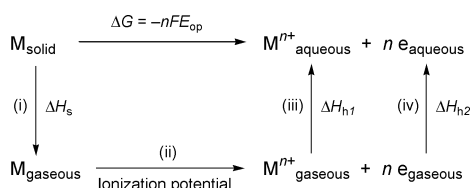
Fig. 1 The wavenumber–diameter profile of SCN⁻ adsorbed at Cu nanorod arrays and the wavenumber–potential profile of SCN⁻ adsorbed at a bulk Cu electrode.

size effect may play an important role on the considerable change of the Fermi energy.

The Fermi level of a metal nanorod can be estimated in a simple way by considering free electrons confined to a cylindrical rod of length l and radius r . The energy level in atomic units is given by:

$$E = \frac{n^2 \pi^2}{l^2} + \frac{C_m^2}{r^2} \quad n = 1, 2, 3, \dots; m = 0, \pm 2, \dots$$

where C_m is a parameter determined by the Bessel function. This equation indicates, at least qualitatively, that the Fermi level of a metal nanorod would increase as the diameter decreases. Since the present study on the Cu nanorods was performed in electrolyte solution, the electrode potential should be calculated under open circuit conditions, where E_{op} corresponds to the Fermi level of a metal nanorod (M_{solid}) in solution. In general, several factors affect the value of E_{op} . These are (i) sublimation of a solid metal, (ii) ionization of a gaseous metal atom, (iii) hydration of a gaseous ion, (iv) hydration of n gaseous electrons; which could be best considered in a Born–Haber type of cycle (Scheme 1).



Scheme 1

For a set of nanorods of the same metal with different diameters, the energy changes for processes of (ii)–(iv) are all the same. Therefore, the differences of the electrode potential E_{op} of a set of nanorods should depend only on the differences of the sublimation energies, ΔH_s . The value of ΔH_s is related directly to the cohesive energy, which is determined by the metal–metal bonding. It is reasonable to assume that the metal–metal bonds are the same in the bulk phase for all the nanorods studied here. However, one has to consider the fact that a surface atom possesses a lower coordinate number as compared to a bulk atom. This implies that the change of the cohesive energy might depend substantially on the ratio of the surface atoms to bulk atoms for nanorods of different size. Based on this, we have carried out the relevant calculations on the potential difference ΔE of a set of nanorods with respect to the bulk electrode potential. Fig. 2 shows the dependence of the potential difference on the diameter ($d = 2r$) of the Cu nanorods. It is clearly seen that the potential difference significantly depends on the nanorod's diameter when the diameter is < 50 nm, and small nanorods show a larger potential difference, indicating an up-shift of the Fermi level. This trend is in general agreement with our experimental results. If we

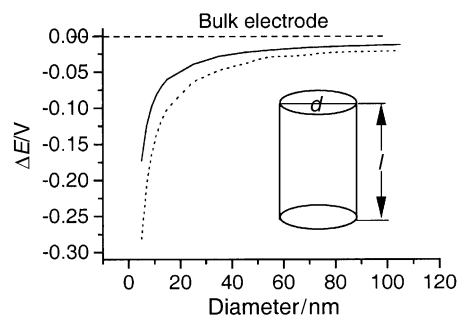


Fig. 2 Dependence with diameter of the difference potential of Cu nanorods ($l \approx 100$ nm) with respect to the bulk Cu electrode after consideration of the surface effect (—) and surface and subsurface effect (.....), see text.

consider the additional influence of the sublayer atoms, the calculated values are even closer to the experimental data. Although more sophisticated theoretical investigation on this aspect is required, it has shown that Raman spectroscopy can be developed into a diagnostic tool for measuring the electronic properties of metal nanorods by applying the probe molecule strategy.

We gratefully acknowledge the financial support from the Natural Science Foundation of China and the Ministry of Education of China. We also sincerely thank D. M. Huang for stimulating discussion.

Notes and references

- 1 C. R. Martin, *Science*, 1994, **266**, 1961.
- 2 J. C. Hulteen and C. R. Martin, in *Nanoparticles and Nanostructured Films*, ed. J. H. Fendler, Wiley-VCH, Weinheim, 1998, ch. 10.
- 3 S. Link, M. B. Mohamed and M. A. Elsayed, *J. Phys. Chem. B*, 1999, **103**, 3073.
- 4 C. K. Preston and M. Moskovits, *J. Phys. Chem.*, 1988, **92**, 2957.
- 5 N. A. F. Al-Rawashdeh, M. L. Sandroock, C. J. Seudling and C. A. Foss, *J. Phys. Chem. B*, 1998, **102**, 361.
- 6 D. Routkevitch, T. L. Haslett, L. Ryan, T. Bigioni, C. Douketis and M. Moskovits, *Chem. Phys.*, 1996, **210**, 343.
- 7 B. B. Li, D. P. Yu and S. L. Zhang, *Phys. Rev. B*, 1999, **59**, 1645.
- 8 A. M. Rao, P. C. Eklund, S. Bandow, A. Thess and R. E. Smalley, *Nature*, 1997, **388**, 257.
- 9 H. Hiura, T. W. Ebbesen, K. Tanigaki and H. Takahashi, *Chem. Phys. Lett.*, 1993, **202**, 509.
- 10 D. A. Weitz, T. J. Gramila, A. Z. Genack and J. I. Gersten, *Phys. Rev. Lett.*, 1980, **45**, 355.
- 11 V. M. Browne, S. G. Fox and P. Hollins, *Catal. Today*, 1991, **9**, 1.
- 12 Z. Q. Tian, B. Ren and B. W. Mao, *J. Phys. Chem. B*, 1997, **101**, 1338.
- 13 S. Shingubara, O. Okino, Y. Sayama, H. Sakaue and T. Tanahagi, *Jpn. J. Appl. Phys.*, 1997 **36**, 7791.
- 14 J. L. Yao, K. H. Xue, B. Ren and Z. Q. Tian, to be submitted.
- 15 Z. Q. Tian, W. H. Li, Z. H. Qiao, W. F. Lin and Z. W. Tian, *Russian J. Electrochem.*, 1995, **31**, 1014.