Journal of Alloys and Compounds 509 (2011) 2016–2020

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

ZnO/Ag heterogeneous structure nanoarrays: Photocatalytic synthesis and used as substrate for surface-enhanced Raman scattering detection

Haibo Hu, Zhenghua Wang*, Sufan Wang, Fengwei Zhang, Suping Zhao, Shiyu Zhu

Anhui Key Laboratory of Functional Molecular Solids, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China

ARTICLE INFO

Article history:
Received 25 July 2010
Received in revised form 14 October 2010
Accepted 22 October 2010
Available online 4 November 2010

Keywords:
Composite materials
Heterojunctions
Nanostructured materials

ABSTRACT

ZnO/Ag composite nanoarrays with heterogeneous structure have been successfully prepared through a photocatalytic method. The adherence of Ag nanoparticles to ZnO nanoarrays was realized through the illumination of visible light, and hence the synthetic method is very simple, economical and low-carbon. Due to their exceptional properties, these composite nanoarrays were used as substrate in surface-enhanced Raman scattering (SERS) measurement. SERS signals of typical analytes such as crystal violet (CV) were observed on Ag nanoparticles from the ZnO/Ag composite nanoarrays, even though the concentration of the analyte was as low as 1×10^{-12} M. The SERS substrate was further applied to detect Sudan dyes (SD II, SD IV), and strong SERS signals were obtained with Sudan dye concentration of 1×10^{-12} M as well. This work provides a new method to prepare SERS substrates for food safety monitoring.

1. Introduction

Nowadays, with the rapid development of economy and society, people have an increasingly high demand of food safety. On one hand, we use more and more food additives in food production; on the other hand, some unethical businessmen sometimes use illegal additives that are harmful to human body in food production. For example, Sudan dyes, including Sudan I, Sudan II, Sudan III and Sudan IV, are a series of artificial dyes and have florid and vivid colors. Due to their excellent properties, they are used extensively in dyeing, plastics, oil paint, waxes, and printing [1,2]. Also, because of their low cost and wide availability, Sudan dyes are illegally added as color additives in food production to enhance and maintain the appearance of food products such as chilli powder and ketchup sauce. However, Sudan dyes are harmful to human beings because they can damage DNA, RNA, some enzymes, and even induce cancer [3,4]. Therefore, Sudan dyes are banned for food usage in most countries [5]. For the sake of food safety, people demand a fast, convenient and reliable method for food additives monitoring. On this point, developing a sensitive, rapid and convenient method for the determination of Sudan dyes is of great significance in food safety monitoring.

Surface-enhanced Raman spectroscopy (SERS) has attracted intense interest since it appeared, because it can enhance Raman scattering intensities by up to 6–8 orders of magnitude [6–9]. SERS has potential application as an ultrasensitive tool to detect chemical and biological molecules [10–14] and further as a method for food safety monitoring. Therefore many scientists put much attention on the fabrication of multifarious SERS substrates.

Various methods for the preparation of SERS substrates have been reported, such as atomic layer deposition (ALD) [15], chemical reduction [16], lithography [17] and ion-beam-sputtered technique [18]. However, more work is still needed to simplify the synthesis method and to improve the sensitivity. In this work, on the basis of previous works about the synthesis of ZnO nanoarrays [19–22], we deposited Ag nanoparticles onto the surfaces of ZnO nanoarrays through a photocatalytic process in which sunshine was applied as the light source. This method is very simple, economical, and low carbon. The ZnO/Ag composite nanoarrays were used as SERS substrate. Typical analytes such as crystal violet (CV) that has been fully characterized by SERS was selected as a model to validate the effect of this substrate. The result indicates that this substrate is valid and ultrasensitive. To further display the potential application of this SERS substrate as a method for food safety monitoring, the SERS substrate was used to detect Sudan dyes (SD II, SD IV) and the SERS signals are strong even though the concentration of Sudan is as low as 1×10^{-12} M. The results show that our work provides a fast, simple and ultrasensitive method to detect Sudan dyes in food safety monitoring.

2. Experimental

All reagents were commercial available from Shanghai Chemical Regents Co. with analytical grade and were used without further purification.

2.1. Synthesis of ZnO nanoarrays

The synthesis was carried out according to a previous report with a little modification [22]. In a typical procedure, 2.97 g Zn(NO3)2·6H2O was dissolved

* Corresponding author. Tel.: +86 553 3869303; fax: +86 553 3869302.
E-mail address: zhwang@mail.ahnu.edu.cn (Z. Wang).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.10.125

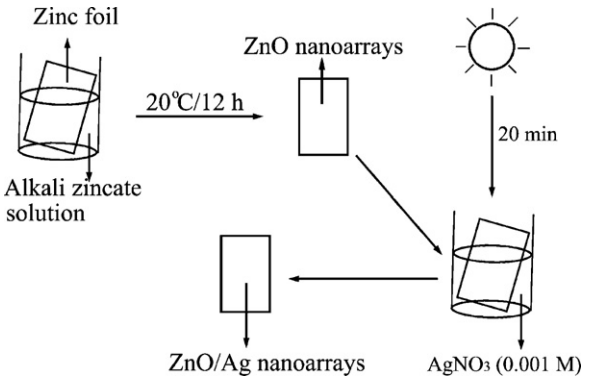

Fig. 1. Synthesis route of ZnO/Ag composite nanoarrays.

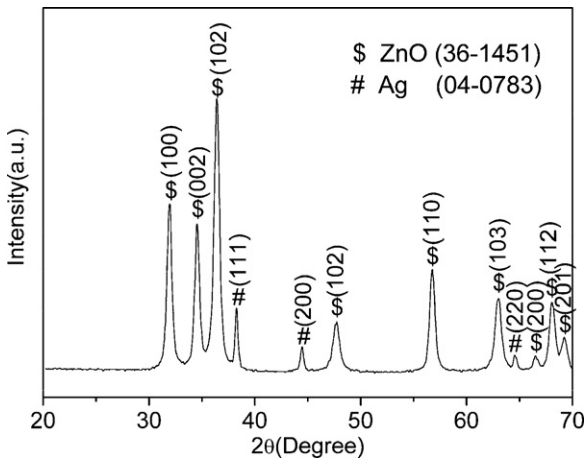

Fig. 2. Typical XRD pattern of the as-obtained ZnO/Ag sample.

in 40 mL deionized water, and then 4.48 g of KOH was added subsequently. The mixture was stirred until the reactants were fully dissolved. Next, a zinc foil (2.5 cm × 4 cm, pretreated by sonication in ethanol and acetone for one time each 5 min and dried with a dry nitrogen stream) was suspended in the solution and the system was sealed in a beaker. After keeping the beaker at 20 °C for 12 h, the zinc foil was taken out and rinsed with de-ionized water and dried for further use.

2.2. Synthesis of ZnO/Ag composite nanoarrays

The ZnO/Ag composite nanoarrays were prepared through a photocatalytic method. First, 40 mL 0.001 M AgNO3 aqueous solution was added into a beaker and

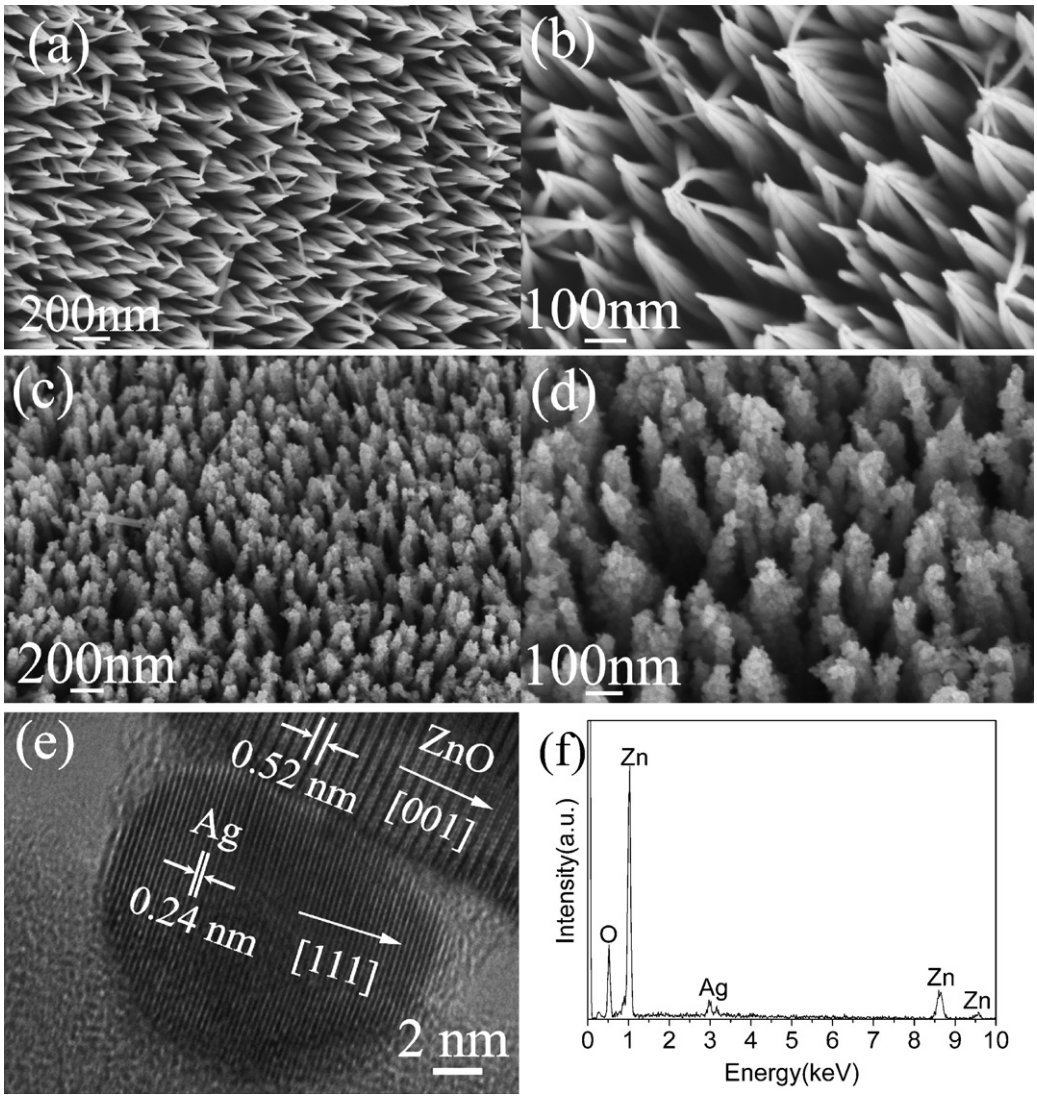

Fig. 3. (a and b) SEM images of ZnO nanoarrays; (c and d) SEM images of ZnO/Ag composite nanoarrays; (e) HRTEM image of ZnO/Ag composite nanoarrays; (f) EDXA spectrum of the ZnO/Ag composite nanoarrays.

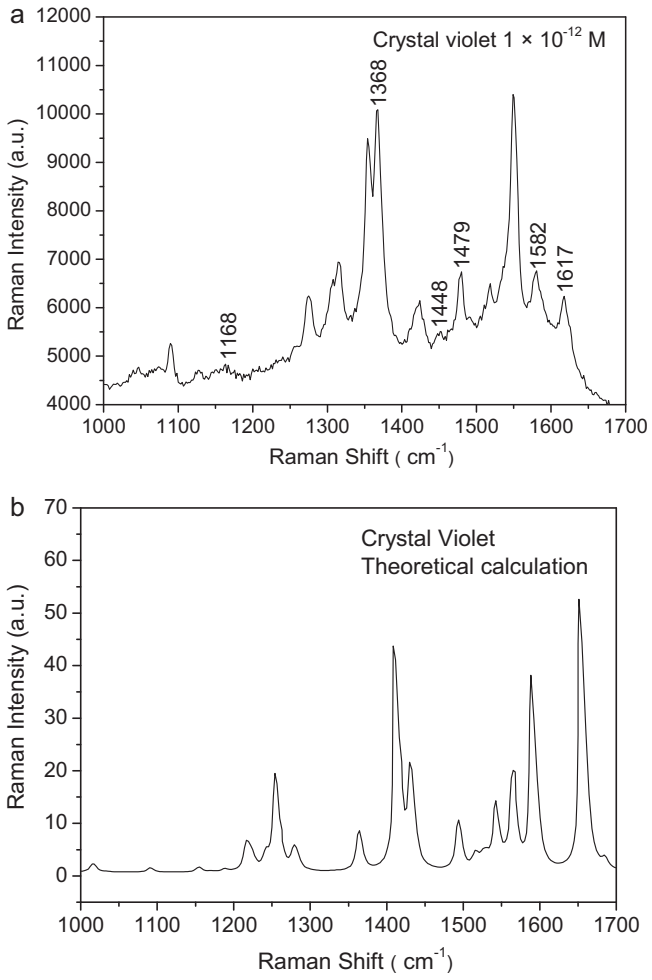

Fig. 4. (a) SERS spectrum of a 1×10^{-12} M CV ethanol solution adsorbed on ZnO/Ag composite nanoarrays; (b) Raman spectrum of CV from theoretical calculation.

then the prepared ZnO nanoarrays were suspended in the solution. The breaker was placed under sunshine for 20 min. After that, the samples was taken out, washed with deionized water several times to remove residual ions and molecules, and dried at 60 °C under vacuum. The whole synthesis procedure is schemed in Fig. 1.

2.3. Characterization methods

The structure and morphology of samples were characterized by X-ray diffraction (XRD; Shimadzu XRD-6000), scanning electron microscopy (SEM; Hitachi S-4800 with energy dispersive X-ray analysis (EDXA) system) and high resolution transmission electron microscopy (HRTEM; Philips, CM200FEG, 200 kV). Crystal violet and Sudan were detected via SERS with a Labram-HR confocal laser micro-Raman spectrometer equipped with an argon ion laser with excitation of 514.5 nm. A piece of ZnO/Ag composite nanoarrays (5 mm × 5 mm) was tailored from the prepared sample. Then the tailored ZnO/Ag composite nanoarrays were affixed to the microscope slides by double-sided adhesive. An air-cooled CCD was used as the detector, the accumulation time was 20 s and the incident power was 3 mW. The spot size of the laser was 1 μm in diameter using a 50× objective.

3. Results and discussion

3.1. Characterization of the obtained samples

The phase and purity of the prepared samples were studied with XRD analysis. Fig. 2 is the typical XRD pattern of the as-obtained ZnO/Ag sample. The diffraction peaks that labeled with "$" could be readily indexed to the hexagonal wurtzite ZnO (JCPDS card No. 36-1451), while those marked with "#" could be indexed to the cubic phase of Ag (JCPDS card No. 04-0783). No other crystalline impurities can be observed. Moreover, the intensity of the diffraction peaks indexed to Ag is comparatively high, which indicates that quite a lot of Ag nanoparticles adhered to the surfaces of ZnO nanoarrays.

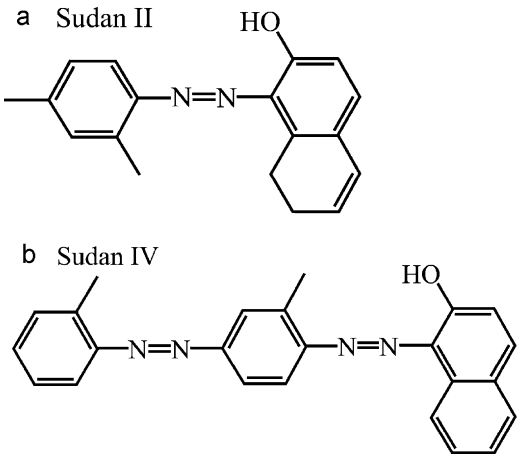

Fig. 5. Chemical structure of Sudan dyes, (a) Sudan II, (b) Sudan IV.

The morphology and size of the as-synthesized samples were examined by SEM. Fig. 3a and b shows the SEM images of the ZnO nanoarrays, from which it can be clearly seen that the surface of the sample is composed of many nanoneedles with a diameter of the needle tips about 6–10 nm. Furthermore, these nanoneedles grew on the zinc foil perpendicularly and their surfaces are smooth. SEM images of the ZnO/Ag sample are shown in Fig. 3c and d, in which we can see that the surfaces of the samples are coarse and many Ag nanoparticles adhered to the surfaces of ZnO nanoarrays. Fig. 3e is the HRTEM image of ZnO/Ag composite nanoarrays, in which we can see that an Ag nanoparticle deposit on the surface of a ZnO nanoneedles. The lattice fringes with interplanar spacing of 0.24 nm correspond to the [1 1 1] crystal plane of Ag nanoparticle, which indicates the high quality of crystallinity. The distance between two crystal lattice fringes in the top of the image is about 0.52 nm, which could be indexed as [0 0 1] crystal planes of ZnO nanoneedle. Fig. 3f is the EDXA spectrum of the ZnO/Ag composite nanoarrays, in which Zn, O and Ag are all present. The EDXA spectrum and HRTEM image both confirm the conclusion that many Ag nanoparticles deposit on the surfaces of ZnO nanoarrays.

3.2. Application of ZnO/Ag composite nanoarrays in SERS

Several groups have reported the detailed SERS of CV which is a typical SERS active analyte [23–25]. The as-obtained ZnO/Ag SERS substrate was firstly used to detect CV to test its effect. The SERS spectrum was obtained by adding 25 μL of CV ethanol solution with a concentration of 1×10^{-12} M on the substrate, as shown in Fig. 4a. There are six characteristic peaks of CV exist in this spectrum. The peaks at 1617, 1582, 1479, 1448, 1368 and 1168 cm^{-1} are all in accordance with the reported values [26]. We also calculated the Raman spectra of CV theoretically using the GAUSSVIEW3.0 program and the theoretical calculation results are shown in Fig. 4b. Although our as-obtained SERS spectra of CV accord with the theoretical calculation results mostly, there are still some obvious differences between the theoretical and the experimental Raman spectra. This phenomenon can be understood easily, because SERS spectrum is not only sensitive to the structure of molecule but also to other factors, such as uniformity of substrate, molecule-to-substrate distance, molecular orientation and so on, none of which have been considered in the calculation. So there will be a few differences between the experimental results and theoretical calculation. In Fig. 4a we can further see that although the con-

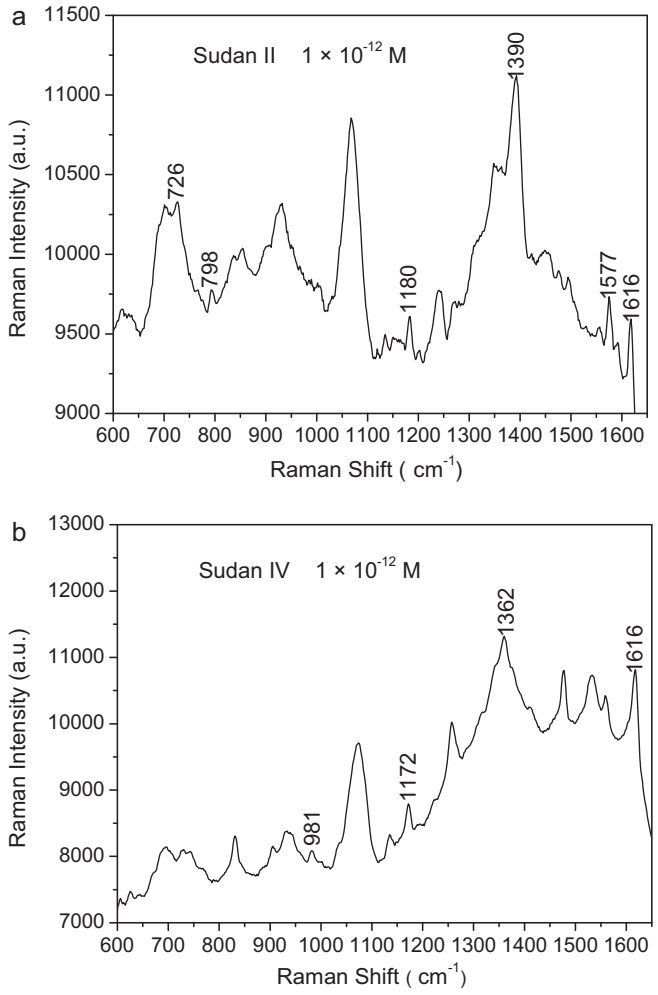

Fig. 6. (a) SERS spectrum of a 1×10^{-12} M Sudan II ethyl acetate solution adsorbed on ZnO/Ag composite nanoarrays; (b) SERS spectrum of a 1×10^{-12} M Sudan IV ethyl acetate solution adsorbed on ZnO/Ag composite nanoarrays.

centration of CV is very much low, the signals of SERS are still very strong. These results indicate that this substrate for SERS-detecting is effective and ultrasensitive.

According to the previous reports [27,28], there are two major mechanisms contribute to the enhancement effect of SERS. The first and foremost is the electromagnetic effect associated with large local fields due to resonances occurring in the microstructures on the metal surface, whose enhancement is believed to be a few orders of magnitude more than the second which is the chemical effect involving a scattering process associated with chemical interaction between the molecule and the metal surface. It is also reported that the smaller metallic particles give higher enhancement [29]. However, when the particle size is less than 15 nm, due to the space between metal nanoparticles being equal to their diameter, the enhancement will saturate. Coincidently, since the Ag nanoparticles coated on ZnO nanoarrays in our work is close to this size, the sensitivity of our SERS substrate is ultrasensitive.

The ZnO/Ag composite nanoarrays were further applied as the SERS substrate to detect Sudan dyes. We selected Sudan II and Sudan IV as the analytes, and their structures are shown in Fig. 5. The SERS spectra were obtained by adding 15 μL of Sudan II, Sudan IV ethyl acetate solution with 1×10^{-12} M concentrations on the substrate, respectively. Fig. 6a and b shows the SERS spectra of Sudan II and Sudan IV, both figures clearly show the characteristic peaks of Sudan dyes. It is noteworthy that due to the slight differences in their chemical structures (Fig. 5), there is little difference between the SERS spectrum of Sudan II and that of Sudan IV. According to previous reports [10,30], the Raman peaks shown in Fig. 6a and b have been assigned. The most prominent peaks around 1390 cm^{-1} and 1362 cm^{-1} are assigned to vibrations of C–N and C=C bonds in the benzene rings. The peak at 1616 cm^{-1} is attributed to the vibrations of N=N bonds and benzene rings. The peak at 1577 cm^{-1} is due to the vibrations of N=N bonds and benzene rings, such as in-plane and out-of-plane bending, symmetric, and asymmetric distortion. The peaks around 1180 cm^{-1} and 1172 cm^{-1} are mainly from C–H bends, benzene rings distortions, and O–H vibrations. The peaks at 726 cm^{-1} and 798 cm^{-1} are from C–H bends, C–O vibrations, and benzene rings breathing. It is noteworthy that the signals of the SERS are still strong even the Sudan II and Sudan IV with a low concentration. These results demonstrate that ZnO/Ag composite nanoarrays can be used as a SERS substrate to detect Sudan dyes (Sudan II, Sudan IV) in concentration as low as 1×10^{-12} M.

4. Conclusions

In summary, ZnO/Ag composite nanoarrays have been successfully synthesized through a photocatalytic method. Due to its especial properties, the ZnO/Ag composite nanoarrays were used as SERS substrates to detect Sudan dyes with a high sensitivity even the concentration is as low as 1×10^{-12} M. The synthetic method of the unique high-efficiency SERS substrate is very simple, economical, low-carbon and free from organic contaminations, which results in higher sensitivity and lower detection limit. Our work provides an effective and convenient method for detecting Sudan dyes at very low concentration, so it may holds promising application prospects in food safety monitoring.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (20701001) and Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering are gratefully acknowledged.

References

[1] C. Westmoreland, D.G. Gatehouse, Carcinogenesis (London) 12 (1991) 1403–1407.
[2] P. Moller, H. Wallin, Mutat. Res. 462 (2000) 13–30.
[3] L.P. Wu, Y.F. Li, C.Z. Huang, Q. Zhang, Anal. Chem. 78 (2006) 5570–5577.
[4] F. Calbiani, M. Careri, L. Elviri, A. Mangia, L. Pistarà, I. Zagnoni, J. Chromatogr. A 1042 (2004) 123–130.
[5] M. Stiborová, V. Martínek, H. Rýdlová, P. Hodek, E. Frei, Cancer Res. 62 (2002) 5678–5684.
[6] S. Nie, S.R. Emory, Science 275 (1997) 1102–1106.
[7] K. Kneipp, Y. Wang, H. Kneipp, L.T. Perelman, I. Itzkan, R.R. Dasari, M.S. Feld, Phys. Rev. Lett. 78 (1997) 1667–1670.
[8] G.C. Schatz, Acc. Chem. Res. 17 (1984) 370–376.
[9] A. Campion, P. Kambhampati, Chem. Soc. Rev. 4 (1998) 241–250.
[10] M.L. Zhang, X. Fan, H.W. Zhou, M.W. Shao, J.A. Zapien, N.B. Wong, S.T. Lee, J. Phys. Chem. C 114 (2010) 1969–1975.
[11] L.M. Chen, L.B. Luo, Z.H. Chen, M.L. Zhang, J.A. Zapien, C.S. Lee, S.T. Lee, Phys. Chem. C 114 (2010) 93–100.
[12] L. Fabris, M. Dante, G. Braun, S.J. Lee, N.O. Reich, M. Moskovits, T.Q. Nguyen, G.C. Bazan, J. Am. Chem. Soc. 129 (2007) 6086–6087.
[13] X.Y. Zhang, M.A. Young, O. Lyandres, R.P. Van Duyne, J. Am. Chem. Soc. 127 (2005) 4484–4489.
[14] R. Malekfar, N. Mohammadian, S. Abbasian, F. Sadeghi, J. Alloy Compd. 488 (2009) 325–327.
[15] X.Y. Zhang, J. Zhao, A.V. Whitney, J.W. Elam, R.P. Van Duyne, J. Am. Chem. Soc. 128 (2006) 10304–10309.
[16] M.W. Shao, M.L. Zhang, N.B. Wong, D.D.D. Ma, H. Wang, W.W. Chen, S.T. Lee, Appl. Phys. Lett. 93 (2008) 233118.
[17] A.V. Whitney, J.W. Elam, P.C. Stair, R.P. Van Duyne, J. Phys. Chem. C. 111 (2007) 16827–16832.

[18] S. Chattopadhyay, H.C. Lo, C.H. Hsu, L.C. Chen, K.H. Chen, Chem. Mater. 17 (2005) 553–559.
[19] A.Z. Hu, F. Wu, J.P. Liu, J. Jiang, R.M. Ding, X. Li, C.X. Cheng, Z.H. Zhu, X.T. Huang, J. Alloy Compd. 507 (2010) 261–266.
[20] A. Qurashi, M.F. Hossain, M. Faiz, N. Tabet, M.W. Alam, N.K. Reddy, J. Alloy Compd. 503 (2010) L40–L43.
[21] L.L. Yang, Q.X. Zhao, M. Willander, J. Alloy Compd. 469 (2009) 623–629.
[22] X.F. Wu, H. Bai, C. Li, G.W. Lu, G.Q. Shi, Chem. Commun. (2006) 1655–1657.
[23] T. Watanabe, B. Pettinger, Chem. Phys. Lett. 89 (1982) 501–507.
[24] Y.C. Chou, N.T. Liang, W.S. Tse, J. Raman Spectrosc. 17 (1986) 481–484.
[25] I. Tsukamoto, K. Machida, J. Raman Spectrosc. 17 (1986) 199–202.
[26] M. Volný, A. Sengupta, C.B. Wilson, B.D. Swanson, E.J. Davis, F. Tureček, Anal. Chem. 79 (2007) 4543–4551.
[27] M.W. Shao, L. Lu, H. Wang, S. Wang, M.L. Zhang, D.D.D. Ma, S.T. Lee, Chem. Commun. (2008) 2310–2312.
[28] A.M. Michaels, M. Nirmal, L.E. Brus, J. Am. Chem. Soc. 121 (1999) 9932–9939.
[29] F.J. García-Vidal, J.B. Pendry, Phys. Rev. Lett. 77 (1996) 1163–1166.
[30] L.S. Zhang, P.X. Zhang, Y. Fang, Anal. Chim. Acta 591 (2007) 214–218.