

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



ZnO/Ag porous Nanosheets used as Substrate for Surface-enhanced Raman Scattering to detect organic pollutant

Kunyu Zhao[†], Jie Lin[†] and Lin Guo^{*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Self-assembled porous ZnO nanosheets were fabricated through an one-step solvent method which is convenient and environment-friendly, and then deposited by the silver nanoparticles to make a type of hybrid materials. The ZnO/Ag composite was used as the substrate for Surface enhanced Raman scattering (SERS) to measure the Rhodamine 6G(R6G) molecules. Strong SERS signals were obtained when the concentration of the probe molecules was as low as 10^{-13} M. Besides, the substrate exhibited light-assisted self-cleaning properties under the UV irradiation. Thus, the as-prepared nanomaterials showed potential application for the organic pollutant detection environment-friendly and economical.

Introduction

As we know, organic pollutants heavily affect the health of human beings, and also damage the growth of plants; therefore, they interfere or destroy the ecological balance seriously.¹⁻⁴ Thus, many researchers has developed a variety of methods to detect the organic pollutants, like the gas chromatography, liquid chromatography and ultraviolet detection.⁵⁻⁷ As one of the developing detection technology of the current analytical chemistry, surface-enhanced Raman scattering (SERS) has attracted more and more attention.

The surface-enhanced Raman scattering, due to its high sensitivity, rapid response, and spectroscopic precision, has been widely used in various fields. SERS holds promising potential not only for chemical, physical, medical, biomolecular sensing, but also for environmental pollution and life science. The Raman cross section is inherently small, comparatively, SERS renders an obviously increase in Raman signals. In order to expand the advantages and application in the detection of organic pollutants, researchers attempt to improve the SERS effects in various nanostructures, obviously, it is necessary to develop a stable SERS substrate to provide a stronger signal enhancement.⁸⁻¹⁰

For many years, noble metal like Au, Ag, Cu nanostructures

were used as traditional SERS substrates, due to the electromagnetic enhancement caused by surface Plasmon resonance mechanism of the metal.¹¹⁻¹⁶ Recently, it has been found that many semiconductors, such as TiO₂, Fe₃O₄, ZnO, also possess SERS activity.¹⁷⁻¹⁹ Particularly, ZnO, as an important semiconductor material with high chemical stability, has a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV. Thus, ZnO has received a great attention, due to its potential applications as the SERS substrates.²⁰⁻²³ For example, Terakawa et al. used the ZnO nanorods as substrate to detect the Raman signals of Rhodamine 6G(R6G) at 532nm, the concentration of detection was as low as $1\mu\text{M}$.²⁴

In recent years, a lot of investigations have been addressed on the huge advantages of using "hybrid materials" as SERS substrates, composite semiconductors (ZnO, and TiO₂) and noble metals (Au and Ag) as the substrates have attracted great attention.²⁵⁻³⁸ According to the previous reports, noble metals possess the SERS activity owing to the electromagnetic enhancement caused by surface Plasmon resonance mechanism.³⁹⁻⁴¹ Whereas, the semiconductors have the SERS activity because of the chemical enhancement, which is caused by the charge transfer between the noble metal and the semiconductor.^{42,43} Recently, several synthesized ZnO/noble metals nanocomposites as the hybrid SERS substrates have also been reported. For example, urchin-like Ag nanoparticle/ZnO hollow nanosphere arrays were fabricated as a SERS substrate, using Rhodamine 6G(R6G) as the probe with the detection limit as low as 10^{-10} M, the enhancement was as high as 10^8 .⁴⁴

Herein, we fabricated a porous ZnO nanosheets decorated with Ag nanoparticles as a hybrid SERS substrate, using

a. School of Chemistry and Environment, Beihang University, Beijing 100191, PR China

E-mail: guolin@buaa.edu.cn

^{*}Corresponding authors

[†]These authors contributed equally to this work

Electronic Supplementary Information (ESI) available. See DOI:

10.1039/x0xx00000x/

Paper

RSC Advances

Rhodamine 6G(R6G) as the SERS active molecule pumped at 532 nm. The limit of detection is as low as 10^{-13} M. The results demonstrate that our work reveals a simple and convenient method to synthesize a hybrid SERS substrate, and the substrate possesses high sensitivity for the potential SERS applications.

Experimental

Chemicals

Zinc acetate dehydrate, sodium hydroxide, silver nitrate, didodecyldimethylammonium bromide (DDAB), ethanol (Beijing Chemical Works), ethylene glycol (Xilong Chemical Co.) were used without any further purification.

Preparation of ZnO Nanosheets

The porous ZnO nanosheets was fabricated through one-step solvent method which is convenient and environment-friendly.⁴⁵ The synthesized porous nanosheets were self-assembled by the ZnO nanoparticles. In this method, the precursor not only acts as the template generators, but also as the building blocks at the same time. The addition of didodecyldimethylammonium bromide (DDAB), was used to achieve better monodispersity of the nanosheets, but did not destroy the growth process. Then, ZnO/Ag nanocomposites were synthesized by the deposition of Ag onto the ZnO nanosheets.

Preparation of ZnO/Ag nanosheets

ZnO/Ag nanocomposites were synthesized by the growth of Ag on the ZnO nanosheets.⁴⁶ Firstly, ZnO production should be heated in a muffle furnace at 500 °C for 2h, in order to make a better crystallinity and stability, and then 30mg ZnO nanosheets was dissolved in ethylene glycol with sonication. 0.5 mL of AgNO₃ (0.01g/mL) aqueous solution was dropped into the ZnO suspension under strong stirring. The dropping rate is about one drop per 30 seconds. The colour of the mixture changed slowly from white to yellow to claybank. After 4 h stirring, the final product was collected, washed with ethanol and deionized water several times, and dried in air at 60 °C for 12 h. Finally, after drying, the production was heated in a nitrogen atmosphere in a quartz tube furnace at 500 °C for 2 h.

Preparation of sample for SERS measurement

For the SERS substrate preparation, ZnO nanosheets were dispersed on a cleaned silicon plate, and the dried silicon was then immersed in R6G ethanol solution for 6 h. The above substrate with sample was rinsed with ethanol several times to make sure no free R6G molecules were left on the surface of the ZnO before Raman measurements.

Materials Characterization

The morphologies of the nanosheets were obtained by scanning electron microscope (SEM, Hitachi S4800 cold field-emission), transmission electron microscope(TEM, JEOL JEM-2100F microscope). The measurements of Raman spectra were characterized with a Jobin Yvon Raman spectrometer model HR800. The 514.5 nm line from an Ar – Kr ion laser and 633 nm line from He – Ne laser were used as excitation source. The laser power on the surface of the sample was typically 1.5 mW. The accumulation time was 10 s.

Results and discussion

The morphology of the as-fabricated ZnO nanosheets was examined by Scanning electron microscopy (SEM) images. From the Fig. 1, we can clearly see the ZnO nanosheets are porous parallelogram with sharp edges. The side length of the ZnO sheets is about 200nm to 600nm, and the thickness is up to 50nm. The surface of the nanosheets is rough. This character is important for the following progress. After the nanosheets were immersed into the AgNO₃ solution, ZnO nanosheets were covered with silver ions, and the silver ions was reduced to Ag nanoparticles after the calcination process, thus, the ZnO/Ag substrate was finally obtained.

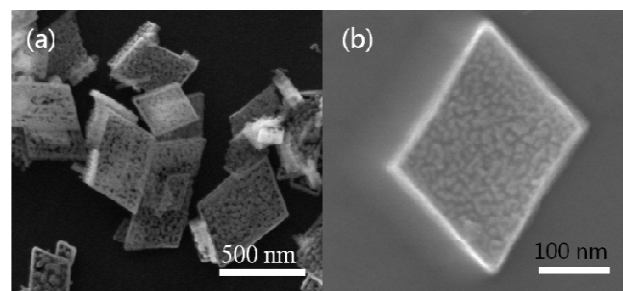


Fig. 1 low-magnification (a) and high-magnification (b) SEM images of the porous ZnO.

From the TEM images of the porous ZnO nanosheets and the ZnO/Ag nanocomposite shown in Fig. 2, we can see the surface of the nanosheets is deposited by the Ag nanoparticles, and we can find that the surface of the ZnO/Ag nanosheets are rougher than that of the pure ZnO nanosheets before deposition. We think the deposition reaction may have certain effect on the morphology of the nanosheets. From the HRTEM image, the interplanar spacing of lattice fringes is 0.283nm and 0.228nm, corresponding to the (100) crystal plane of ZnO nanoparticle and (111) crystal plane of Ag nanoparticle. We also found that the distance between the Ag nanoparticles is less than 10 nm (Fig. S2).

Fig. 3 shows the EDS spectrum of the ZnO/Ag hybrid nanosheets, in which we can see that Zn, O and Ag are all presented, demonstrating that Ag nanoparticles mixed well

with ZnO nanosheets. According to the EDS spectrum and

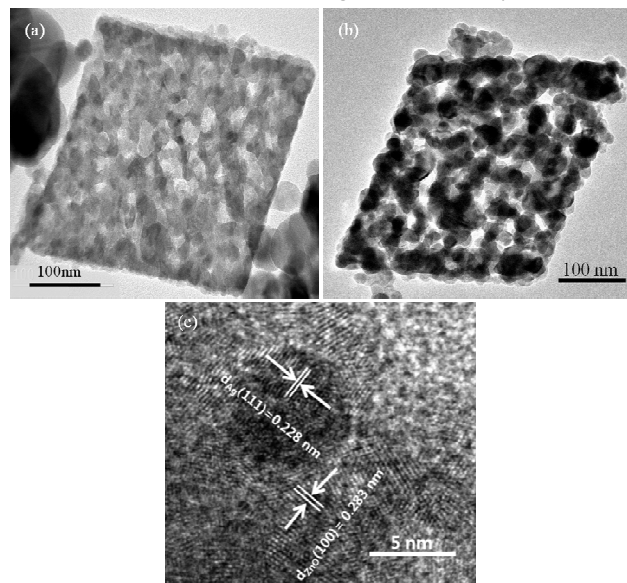


Fig. 2 (a-b) TEM images of the porous ZnO nanosheets and the ZnO/Ag nanocomposites; (c) HRTEM image of the ZnO/Ag nanocomposites.

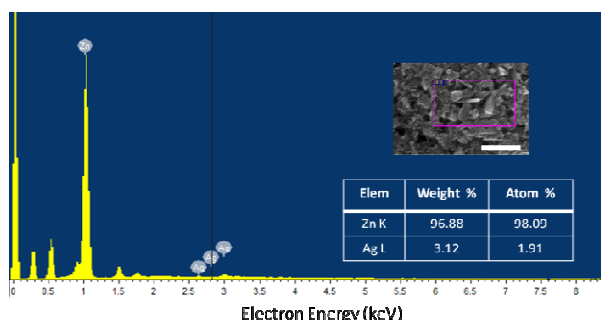


Fig. 3 EDS spectra of the obtained ZnO/Ag nanocomposite.

HRTEM image, the good deposition of Ag nanoparticles on the surface of ZnO nanosheets can be well confirmed.

We measured the UV-vis diffuse reflection spectrum of porous ZnO nanosheets and ZnO/Ag nanocomposite. As shown in Fig. 4. The ZnO nanosheets showed an appreciable peak at 365 nm, and the reflectance of the ZnO/Ag nanocomposite has been improved in the visible region. There was an unobvious peak from 400 nm to 500 nm, which could be assigned the transverse Plasmon mode of Ag nanoparticles. The improvement was not obvious because of the light concentration of the Ag nanoparticles.

The porous ZnO nanosheet and ZnO/Ag nanocomposite material was used as substrate to detect the SERS activity. R6G probe molecule was used to analysis the difference of the two SERS substrate. As shown in Fig. 5, the ZnO/Ag nanocomposite presented a high enhancement compared with the porous ZnO nanosheets. As a potential substrate, the hybrid composite substrate should reveal high sensitivity and stability. In our SERS experiment, the SERS spectrum of R6G probe molecule

absorbed on ZnO/Ag substrate clearly distinguish characteristic bands at 1×10^{-13} M concentration as shown in Fig. 6 Band around 611 cm^{-1} is assigned to out-of-plane deformation vibration of the xanthene ring, vibrations at 1360 cm^{-1} and 1648 cm^{-1} are assigned to in-plane stretch vibrations of the xanthene ring. The result indicates ZnO/Ag nanocomposite have significant SERS effect in molecule detection.

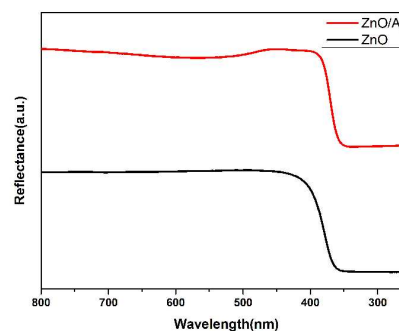


Fig. 4 UV-vis diffuse reflection spectrum of porous ZnO nanosheets (black line) and ZnO/Ag nanocomposite (red line)

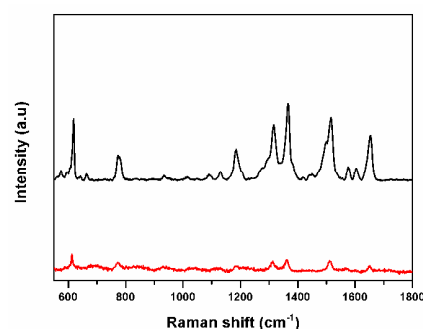


Fig. 5 the SERS spectra of R6G detected by porous ZnO nanosheets (black) and ZnO/Ag nanocomposite (red)

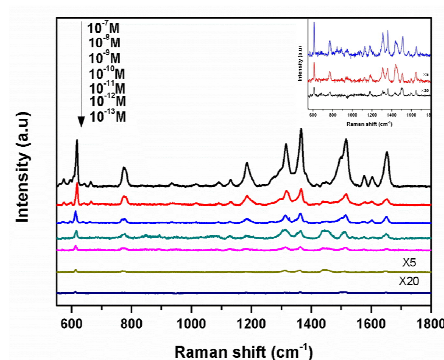


Fig. 6 SERS spectra of R6G on ZnO/Ag nanocomposite substrate with different various concentrations. The inset picture is the SERS spectra of the low concentration (10^{-11} M , 10^{-12} M , 10^{-13} M). Excitation wavelength: 633 nm; power: 1.5 mw; lens: 50 X long distance objective; acquisition time: 10 S.

Paper

RSC Advances

The enhancement mechanism for semiconductor – noble metal substrate has been reported in many literatures, there are two main explanations for the mechanism: (i) Fermi level of noble material is doped into band gap of the semiconductor, served as doping level, accelerating charge-transfer process. (ii) Semiconductor acts as a template for noble metal nanoparticles, adjusting and controlling the effect of near-field coupling between nanoparticles, aiming at forming more “hot spots” for high enhancement of SERS scattering. The second mechanism is dominant for the high sensitivity in SERS experiment, because the low concentration (1×10^{-13} M) can be detected by Ag nanoparticles, which serves as many “hot spots”.⁴⁷

By comparing the SERS signals from the 10^{-7} M and 10^{-13} M in Fig. 6, clear difference in peak intensity is observed, which can be explained by the following three reasons. i) Raman signal comes from the relaxation process when the molecules come back from the excited state to the ground state, which is a nonradiative process by phonons. However, at low concentration of R6G, only several molecules can stimulate the SERS signal, different transition channels result in nonreproducible Raman signal. (ii) The SERS enhancement is not only contributed by well – documented electromagnetic “hot spot”, but also influenced by the chemical interactions of ground state and dynamic charge transfer process. (iii) Raman signal enhancement is significantly high when Probe molecule absorbed at “hot spot”, nonlinear optics processes will take Raman active molecules to the semi-state, switching Raman signal off and resulting in the blinking or peak splitting phenomenon as shown in Fig. 6 (10^{-7} M; 1507cm^{-1}). In addition, SERS signal enhanced by 514.5 nm laser wavelength is weaker than 633 nm (Fig. S1), which can be explained by the surface plasma excitation of Ag nanoparticles under laser irradiation, making electron transfer from Ag to ZnO and forming plenty of electron hole and electron pairs. These well-separated electron-hole pairs will photochemically decompose the probe molecule absorbed on Ag surface, which in turn reducing Raman signal at 514.5 nm laser excitation.

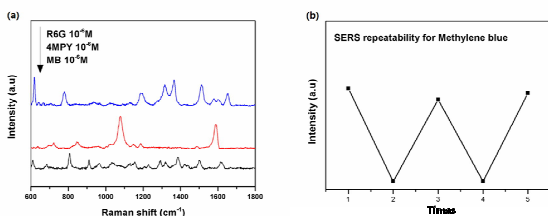


Fig. 7 (a) Recycle SERS experiment of three different molecules absorbed on ZnO/Ag substrate by self-cleaning under UV irradiation. (b) SERS response of Methylene blue molecule (peak signal at 1620cm^{-1}) under repeated UV irradiation. Laser wavelength: 633nm; power: 1.5mw; lens: 50X long distance objective; acquisition time: 2 S.

Except for acting as an effective SERS substrate, ZnO/Ag nanocomposite also exhibited light-assisted self-cleaning properties. The mechanism for self-cleaning activity under UV irradiation can be described as follows: Charge-transfer process from ZnO to Ag excited by UV light would produce highly active oxidative species ($\bullet\text{O}_2^-$, $\bullet\text{OH}$) on the surface of porous ZnO nanosheets, decomposing the absorbed probe molecules on the surface of ZnO/Ag composite.^{48,49} Three different molecules absorbed on ZnO/Ag composite are successfully decomposed one after another by UV irradiation and the SERS effect of the substrate is remained effective, which is clearly illustrated in Fig. 7(a). To further investigate the relationship between the self-cleaning property and the substrate SERS activity, Fig. 7(b) shows the ZnO/Ag substrate could be regenerated without loss of SERS activity by self-cleaning performance under the UV irradiation. In situ recycling SERS mapping of ZnO/Ag substrate absorbed by 4-MBA (the peak mapped is 1586cm^{-1}) and Methyl blue is shown in Fig. S2, which confirms the composite material is a kind of easily recyclable and highly efficient SERS materials.

Conclusions

In conclusion, a simple and convenient method was used to fabricate the self-assembly porous ZnO nanosheets, and the ZnO/Ag nanosheets were deposited by the silver nanoparticles to make hybrid materials for the Surface enhanced Raman scattering (SERS) applications. Raman analyses showed that the ZnO/Ag composite nanosheets are highly SERS active substrates to measure the Rhodamine 6G(R6G) molecules. The enhancement factor was as high as 10^8 when the concentration of the probe molecules was as low as 10^{-13} M. The SERS effects is not only contributed by electromagnetic “hot spot”, but also influenced by the chemical interactions of ground state and dynamic charge transfer process. Besides, the substrate exhibited light-assisted self-cleaning properties under the UV irradiation. The recyclability of the substrate makes the SERS detection more environment-friendly and economical, showing great potential in the detection of organic pollutants and life science.

Acknowledgements

The project was supported by the National Natural Science Foundation of China (51272012 & 21471013)

References

- 1 Z. Aksu, *Process Biochem.*, 2005, **40**, 997.
- 2 R. A. Hites, *Environ. Sci. Technol.*, 2004, **38**, 945.
- 3 D. W. Kolpin, E. T. Furlong, M. T. Meyer, E. M. Thurman, S. D. Zaugg, L. B. Barber and H. T. Buxton, *Environ. Sci. Technol.*, 2002, **36**, 1202.

- 4 J. P. Giesy and K. Kannan, *Environ. Sci. Technol.*, 2001, **35**, 1339.
- 5 Z. Zhang, Z. Lei, Z. Zhang, N. Sugiura, X. Xu and D. Yin, *J. Hazard. Mater.*, 2007, **149**, 657.
- 6 P. Westerhoff, H. Moon, D. Minakata and J. Crittenden, *Water Res.*, 2009, **43**, 3992.
- 7 X. Zhu, J. Ni, J. Wei, X. Xing and H. Li, *J. Hazard. Mater.*, 2011, **189**, 127.
- 8 G. Shan, S. Zheng, S. Chen, Y. Chen and Y. Liu, *Colloids Surf. B.*, 2012, **94**, 157.
- 9 H. Tang, G. Meng, Q. Huang, Z. Zhang, Z. Huang and C. Zhu, *Adv. Funct. Mater.*, 2012, **22**, 218.
- 10 A. O. Dikovska, N. N. Nedyalkov, S. E. Imamova, G. B. Atanasova and P. A. Atanasov, *Quantum Electronics*, 2012, **42**, 258.
- 11 Y. H. Jang, K. Chung, L. N. Quan, B. Spackova, H. Sipova, S. Moon, W. J. Cho, H. Y. Shin, Y. J. Jang, J. E. Lee, S. T. Kochuveedu, M. J. Yoon, J. Kim, S. Yoon, J. K. Kim, D. Kim, J. Homola and D. H. Kim, *Nanoscale*, 2013, **5**, 12261.
- 12 J. Tang, Y. Yi, J. Wu and Y. Tang, *Physica B*, 2014, **433**, 138.
- 13 N. G. Tognalli, E. Cortés, A. D. Hernández-Nieves, P. Carro, G. Usaj, C. A. Balseiro, M. E. Vela, R. C. Salvarezza and A. Fainstein, *ACS Nano*, 2011, **5**, 5433.
- 14 S. E. J. Bell and M. R. McCourt, *Phys. Chem. Chem. Phys.*, 2009, **11**, 7455.
- 15 M. A. Mahmoud, C. E. Tabor, M. A. El-Sayed, *J. Phys. Chem. C*, 2009, **113**, 5493.
- 16 Y. Tanoue, K. Sugawa, T. Yamamuro and T. Akiyama, *Phys. Chem. Chem. Phys.*, 2013, **15**, 15802.
- 17 X. Fu, G. Zhang, T. Wu and S. Wang, *Can. J. Chem.*, 2013, **91**, 1112.
- 18 Z. Sun, B. Zhao and J. R. Lombardi, *Appl. Phys. Lett.*, 2007, **91**, 221106.
- 19 X. Zhou, W. Xu, Y. Wang, Q. Kuang, Y. Shi, L. Zhong and Q. Zhang, *J. Phys. Chem. C*, 2010, **114**, 19607.
- 20 T. Sakano, Y. Tanaka, R. Nishimura, N. N. Nedyalkov, P. A. Atanasov, T. Saiki and M. Obara, *J. Phys. D: Appl. Phys.*, 2008, **41**, 235304.
- 21 S. Lee, J.-W. Peng and C.-S. Liu, *Appl. Surf. Sci.*, 2013, **285**, 748.
- 22 Z. Mao, W. Song, X. Xue, W. Ji, L. Chen, J. R. Lombardi and B. Zhao, *J. Phys. Chem. C*, 2012, **116**, 26908.
- 23 Y. Wang, W. Ruan, J. Zhang, B. Yang, W. Xu, B. Zhao and J. R. Lombardi, *J. Raman Spectrosc.*, 2009, **40**, 1072.
- 24 M. Terakawa, Y. Tanaka, G. Obara, T. Sakano and M. Obara, *Appl. Phys. A*, 2010, **102**, 661.
- 25 X. He, C. Yue, Y. Zang, J. Yin, S. Sun, J. Li and J. Kang, *J. Phys. Chem. A*, 2013, **1**, 15010.
- 26 Z. Sun, C. Wang, J. Yang, B. Zhao and J. R. Lombardi, *J. Phys. Chem. C*, 2008, **112**, 6093.
- 27 L. Chen, L. Luo, Z. Chen, M. Zhang, J. A. Zapien, C. S. Lee and S. T. Lee, *J. Phys. Chem. C*, 2010, **114**, 93.
- 28 X. Zhao, B. Zhang, K. Ai, G. Zhang, L. Cao, X. Liu, H. Sun, H. Wang and L. Lu, *J. Mater. Chem.*, 2009, **19**, 5547.
- 29 J. Yin, Y. Zang, C. Yue, Z. Wu, S. Wu, J. Li and Z. Wu, *J. Mater. Chem.*, 2012, **22**, 7902.
- 30 F. Xu, Y. Zhang, Y. Sun, Y. Shi, Z. Wen and Z. Li, *J. Phys. Chem. C*, 2011, **115**, 9977.
- 31 W. Song, Y. Wang, H. Hu and B. Zhao, *J. Raman Spectrosc.*, 2007, **38**, 1320.
- 32 W. Song, X. Han, L. Chen, Y. Yang, B. Tang, W. Ji, W. Ruan, W. Xu, B. Zhao and Y. Ozaki, *J. Raman Spectrosc.*, 2010, **41**, 907.
- 33 G. Sinha, L. E. Depero and I. Alessandri, *ACS Appl. Mater. Inter.*, 2011, **3**, 2557.
- 34 X. Liu, F. Li, Y. Wang, H. Jin, H. Wang and Z. Li, *Mater. Lett.*, 2013, **94**, 19.
- 35 C. Y. Liu, M. M. Dvoynenko, M. Y. Lai, T. H. Chan, Y. R. Lee, J. K. Wang and Y. L. Wang, *Appl. Phys. Lett.*, 2010, **96**, 033109.
- 36 L. L. Limiao Chen, Zhenhua Chen, Mingliang Zhang, Juan Antonio Zapien, Chun Sing Lee, and Shuit Tong Lee, *J. Phys. Chem. C*, 2010, **1**, 93.
- 37 H. Hu, Z. Wang, S. Wang, F. Zhang, S. Zhao and S. Zhu, *J. Alloys Compd.*, 2011, **509**, 2016.
- 38 Z. Mao, W. Song, X. Xue, W. Ji, Z. Li, L. Chen, H. Mao, H. Lv, X. Wang, J. R. Lombardi and B. Zhao, *J. Phys. Chem. C*, 2012, **116**, 14701.
- 39 M. V. Cañamares, J. V. Garcia-Ramos, J. D. Gómez-Varga, C. Domingo and S. Sanchez-Cortes, *Langmuir*, 2005, **21**, 8546.
- 40 T. Y. Olson, A. M. Schwartzberg, C. A. Orme, C. E. Talley, B. O'Connell and J. Z. Zhang, *J. Phys. Chem. C*, 2008, **112**, 6319.
- 41 M. Rycenga, M. H. Kim, P. H. C. Camargo, C. Cobley, Z.-Y. Li and Y. Xia, *J. Phys. Chem. A*, 2009, **113**, 3932.
- 42 K. Kim, K. L. Kim and K. S. Shin, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9288.
- 43 W. Song, Y. Wang and B. Zhao, *J. Phys. Chem. C*, 2007, **111**, 12786.
- 44 X. He, C. Yue, Y. Zang, J. Yin, S. Sun, J. Li and J. Kang, *J. Mater. Chem. A*, 2013, **1**, 15010.
- 45 Q. Liu, L. Jiang and L. Guo, *Small*, 2014, **10**, 48.
- 46 G. Xi, J. Ye, Q. Ma, N. Su, H. Bai and C. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 6508.
- 47 Y. Fang, N. Seong, D. D. Dlott, *Science*, 2008, **321**, 388.
- 48 Y. Zhou, J. Chen, L. Zhang and L. Yang, *Eur. J. Inorg. Chem.*, 2012, 3176.
- 49 R. Dastjerdi, M. Montazer, S. Shahsavan, *Colloids Surf. B.*, 2010, **81**, 32.