Analyst Accepted Manuscript



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. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it 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 <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> 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.



www.rsc.org/analyst

6 7 8

9 10

11

12

13 14

15

16

17

18

19

20

21

22

23 24 25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59 60

Analyst

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Single-particles of NaYF4:Yb,Er@Ag enhanced Raman scattering and plasmonic photocatalysis under near-infrared laser excitation

Yongmei Ma, Honglin Liu,* Zhenzhen Han, Liangbao Yang,* Bai Sun, and Jinhuai Liu

This study reports the significantly improved Raman enhancement and plasmon photocatalytic ability of silver nanoparticles (Ag NPs) by decorating them on single NaYF4:Yb,Er upconversion (UC) microcrystal under near-infrared excitation. This sheds new light on applications of UC-noble metal composites and also promises a novel direction for fabricating SERS-active nanostructures.

Introduction

Surface-enhanced Raman scattering (SERS), widely used in many detection fields, can provide excellent fingerprint information and high sensitivity.¹⁻³ Its performances usually depend on many factors, particularly, strongly relying on an external excitation light source.⁴ It is noted that the excitation lasers used in most SERS studies are UV/visible lights^{5, 6} which can facilely match the localized surface plasmon resonance (LSPR) frequencies of noble metal nanostructures.⁷⁻¹⁰ But the UV/visible light has shorter sample penetration depths and the high laser power can result in a strong heating effect easier, both of these will restrict their prospects as luminescent stains in bio-imaging.¹¹ Generally, the laser with longer wavelengths will have much deeper penetration depth, e.g. the near-infrared (NIR) lights.¹² One has to tune the LSPR features of nanostructures through complex assembly to match the NIR excitation for the purpose of high SERS sensitivity.13, 14 To date, it remains a great challenge to facilely fabricate nanostructures whose LSPR can match well the NIR excitation and generate perfect SERS enhancement under relatively lower level of laser power. Interestingly, UC materials can convert two or more low-energy pump photons to a higher-energy output photon,^{15,} ¹⁶ which provide the possibility to overcome the above problems. Recently, the coupling of UC nanocrystals with noble metal NPs such as Ag and Au has been developed as a valuable strategy to enhance their luminescence,^{17, 18} of which the intrinsic mechanism might be similar to the LSPR-related Raman enhancement. However, few examples of UC materialrelated SERS have been reported and its mechanism remains ambiguous.

Herein, we speculate that the incorporation of UC materials into SERS-active nanoparticles might provide a new light into the role of UC materials in Raman enhancement and plasmon photocatalysis. As shown in scheme 1, under the NIR excitation of 785 nm, the Yb³⁺ ions act as sensitizers and are the primary absorbers of the NIR excitation. Then Yb³⁺ will transfer the energy absorbed from the NIR excitation to Er³⁺, the Er³⁺ ions are excited from the ${}^{4}I_{15/2}$ ground state to the ${}^{4}I_{11/2}$ excited state via Yb³⁺ \rightarrow Er³⁺ energy transfer. The luminescent states of Er³⁺ are excited by two consecutive $Yb^{3+} \rightarrow Er^{3+}$ energy transfer events, the first energy transfer is the ${}^{4}I_{15/2}$ ground state, and the second energy transfer is the long-lived intermediate excited state (i.e., ${}^{4}I_{13/2}$ or ${}^{4}I_{11/2}$). Then the Er³⁺ ion is excited to the ${}^{4}F_{7/2}$ state by a second $Yb^{3+} \rightarrow Er^{3+}$ energy transfer. After that, the Er^{3+} ion decays nonradiatively to the ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ levels, which gives the dominant green luminescence $({}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2})$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$) and red emission is obtained by the transition ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ (inset in Fig.1B). ¹⁹⁻²² In the presence of noble metals NPs, such as Au or Ag NPs, the broad absorption of noble metals can increase the power of the excitation by local field enhancement, resulting in the increase of excited Yb3+ ions, and more energy transfers from excited Yb³⁺ to Er³⁺.²³ The highly enhanced local field density will act on the SERS effects, resulting in the dramatically increased strengths of plasmon photocatalysis. In addition, the UC emission materials convert the NIR radiation into green emissions with bands at 520, 528 and 540 nm which are close to the LSPR peak of Ag, resulting in significantly EM fields rise at the noble metal surface and consequently amplify the Raman scattering. These analysis were nicely supported by excellent improvement on Raman enhancement and photocatalytic ability in following experiments.

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60



Scheme 1. Illustration of the relevant processes of energy transfer in UC@Ag particles and the local electric field, ELSPR, enhanced by the LSPR of Ag NPs. ("ETU" is short for energy transfer upconversion and "CET" is short for cooperative energy transfer.)

Experimental Section

Chemicals and Materials

Silver nitrate (AgNO₃), sodium citrate, para-aminothiophenol (PATP), NaF, ErCl₃, YbCl₃.6H₂O, YCl₃.6H₂O, Ethylene Diamiane Tetraacetic (EDTA), and all of these were A.R. grade and obtained from Shanghai Reagent Co. without further purification, and their solutions were prepared with distilled water without further pH regulation. The whole experiment was carried out in water system without any buffer, and the all experiments under room temperature (25° C).

Synthesis of upconversion material

NaYF4:Yb,Er NCs were synthesized by a simple hydrothermal method using trisodium citrate as a capping agent.¹ An aqueous solution of YCl₃.6H₂O, YbCl₃.6H₂O and ErCl₃ (lanthanide ion molar ratio, Y/Yb/Er = 88:10:2) was mixed with an aqueous solution of trisodium citrate under vigorous stirring resulting in a white complex. Then an aqueous solution of NaF was added into the complex and stirred for 1 h. The newly-formed complex precursor solution was then transferred into a 60 ml autoclave and heated at 180°C for 3 h. The NaYF4:Yb,Er NCs were then separated via centrifugation and rinsed several times with ultrapure water.

Ag coating of the upconversion material

The Ag NCs attached onto the NaYF4:Yb,Er NCs was performed by using trisodium citrate as a coupling agent and a reductant. The dryed NaYF4:Yb,Er NCs were redispersed in ultrapure water, and AgNO₃ solution was added into the solution, and then the mixture solution was stirred and heated to 100 °C. Then the trisodium citrate solution was added into the boiling solution, keep the temperature of the mixed solution for 1 hour. The obtained products were centrifugally precipitated, and rinsed several times with ultrapure water.

Synthesis of Ag NPs

Ag NPs were prepared by citrate reduction of AgNO₃.² 1 ml 0.1 M AgNO₃ was added into 99 ml ultra-pure water, and then the solution was brought to a vigorous boil with stirring in a round bottom flask fitted with a reflux condenser and heated to 100 °C. 10g/L trisodium citrate (4 ml) was then added rapidly to the solution, keep the temperature of the mixed solution for 1 hour. The obtained products were centrifugally precipitated, and rinsed several times with ultrapure water.

Apparatus

The scanning electron microscopy (SEM) images were taken by a Sirion 200 field-emission scanning electron microscope. X-Ray scattering patterns were conducted by analyzing the powder samples on a Philips X-Pert Pro X-ray diffractometer (XRD) with Cu Ka radiation. Transmission electron microscopy (TEM) images were recorded by a JEOL 2010 high resolution transmission electron microscope, equipped with Xray energy dispersive spectroscopy (EDS) capabilities, operated at an acceleration voltage of 200 kV. Upconversion luminescence spectra were recorded by using a fluorescence spectrophotometer under the excitation of a 980 nm laser. Raman spectra were carried out on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) using an Ar ion laser operating at 785 nm. The laser power was approximately 1 mW. All of the spectra reported were the results of a single 1 s accumulation.

Results and Discussion

The hexagonal NaYF4:Yb,Er microcrystals with the uniform size and shape were successfully synthesized by a simple hydrothermal method, their average side length is ~600 nm. Then a simple procedure was developed to decorate highdensity Ag NPs on the surface of this microcrystal ((Fig. 1A-B). Single-particle of NaYF4:Yb,Er@Ag microcrystals (labeled as UC@Ag) was used to investigate their Raman enhancement and plasmon photocatalysis behaviors under NIR excitation with a relatively low laser power. The HRTEM at high angle annular dark field (HAADF) evidenced that all the elements of Ag, Yb, and Er distributed throughout the entire particle (Fig. 1). The statistical diameters of these Ag NPs were mainly in the range of 45±13 nm. (Fig. S3A). The LSPR peak of the Ag NPs decorated on NaYF4:Yb,Er located at ~405 nm, it doesn't red shift deducting the broad absorption of UC (Fig. S3B-C). As a reference, the closely-packed multilayer of pure Ag nanoparticles (labeled as ML-Ag) were measured, the interparticle gap among ML-Ag was less than 5 nm (Fig. S4A-B) that can maximize the localized electric field and greatly amplify the Raman signals of target molecules.^{24, 25} In contrast, the distribution of those Ag NPs decorated on NaYF4:Yb,Er microcrystal was relatively sparse (Fig. 1A and B) and their

~

nalyst Accepted Manusc

interparticle gaps were much larger than that of ML-Ag. Due to the confinement of our SERS experimental setups, a 785 nm laser was selected as the excitation light.

Analyst



Figure 1. (A) SEM and (B) TEM imagine of UC@Ag (inset: the corresponding emission spectrum of UC@Ag). (C–E) The elemental mapping of a single particle of UC@Ag from the HRTEM images, based on the Ag La1, Yb La1 and Er La1.



Figure 2. SERS spectra of 10^{-6} M pATP adsorbed on (A) a single particle of UC@Ag and (B) the ML-Ag with the excitation laser of 785nm and the integration time of 5 s. (C) A series of SERS spectra of 10^{-6} M pATP molecules collected on 50 randomly selected particles of the UC@Ag and (D) the intensities at 1142 cm⁻¹ of pATP.

To verify the SERS capability of UC@Ag, a series of experiments were carried out by the use of 4-aminothiophenol (pATP) as the signal reporter under 785 nm excitation laser.²⁶ We firstly demonstrated that the absorbed pATP will be transformed to DMAB under a high-power laser ang the Raman signals of the " b_2 modes" are actually contributed by the a_g mode of DMAB. As shown in Fig. 2B, the intensity of the 1142cm⁻¹ peak is only about 700 cnts produced by the ML-Ag. The corresponding SERS intensity of the 1142cm⁻¹ peak of pATP adsorbed on UC@Ag is about 35000 cnts as shown in Fig. 2A, which is nearly 50 times larger than that obtained on

ML-Ag. As mentioned above, the shape, LSPR and size of the Ag NPs decorated on NaYF4:Yb,Er were similar to that of the pure Ag NPs. More importantly, the interparticle gaps among the Ag NPs decorated on NaYF4:Yb,Er were larger than that of the ML-Ag. So the Ag NPs modified on NaYF4:Yb,Er cannot enhance one order of magnitude SERS intensity of analyte in comparison to ML-Ag. Therefore, it should be the presence of UC materials that contributed to the greatly improved SERS performance of UC@Ag as shown in scheme 1. The intensity of the main vibration of pATP from 50 particles of SERS data shown in Fig. 2C indicated the excellent reproducibility, further evidenced by a statistical relative standard deviation (RSD) of Raman intensity at 1142 cm⁻¹ (Fig. 2D).¹¹ And different batches of SERS substrate also indicated a good reproducibility (Fig. S5).

To prove the sensitivity of UC@Ag substrate, SERS spectra of pATP were collected by varying its concentration from 10⁻⁵ to 10⁻⁹ M, as shown in Fig. 3A. The intensity of the strongest peak at 1142 cm⁻¹ was used for the quantitative evaluation of the detection level and exhibited a good linear relationship with the concentration ranging from 1.0×10^{-5} to 1.0×10^{-9} M (R² = 0.98), as shown in Fig. 3D. The limit of detection was determined to be 1.0×10^{-9} M from three standard deviations above the background. As a comparison, Fig. 3C showed the SERS spectra of pATP with different concentrations were also collected on ML-Ag. As shown in Fig. 3D, the Raman intensity at 1142 cm⁻¹ with the logarithm of pATP concentrations cab be fitted by a linear plot well ($R^2 = 0.99$). The limit of detection was determined to be 5.0 \times 10⁻⁷ M from three standard deviations above the background, so the sensitivity of UC@Ag substrate is about 3 orders of magnitude lower than ML-Ag substrate.



Figure 3. SERS spectra obtained from different concentrations of pATP using (A) UC@Ag and (C) ML-Ag substrates under 785 nm. (B) and (D) are the linear correlation of Raman intensity at 1142 cm⁻¹ with the logarithm of pATP concentrations.

Although we have dealt with the consistency of Ag particles on the two SERS substrates, the comparison of SERS enhancement between two different substrates is still

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53 54

55

56

57

58 59 60

unconvincing. So the SERS enhancement effects of a fixed position on the same substrate were examined under two different excitation lasers, 785 nm and 532 nm, respectively. A same area of the UC@Ag substrate excited by these two different lasers exhibited different SERS enhancements (Fig. 4 A and B). The excitation laser of 785 nm produced a strong SERS signal with a maximum strength of 23000 cnts at 1072 cm⁻¹ (curve b in Fig.4A). In contrast, the excitation laser of 532 nm produced a much stronger SERS signal with a maximum strength of 47000 cnts at 1072 cm⁻¹ (curve a in Fig.4A). Hence, the laser wavelength-dependent enhancement sensitivities (Es) can be estimated by the comparison of the intensities of the 1072 cm⁻¹ band using the equation: Es = $I/(C \times M)$, I is the intensity of pATP, C is the concentration of pATP and M is the amounts of the substrates, C and M are the same in two different experiments.²⁷ It can be estimated that the enhancement effect of 532 nm is only ~2.1 times that of 785 nm on the UC@Ag substrate (Fig.4B). Similarly, the enhancement effects of ML-Ag under two excitation lasers, 785 nm and 532 nm, were also examined, respectively. Fig.4C illustrated that the excitation laser of 785 nm produced a relatively weak SERS signal with a maximum strength of 700 cnts at 1072 cm⁻¹ (curve b in Fig.4C). In contrast, the excitation laser of 532 nm produced a much stronger SERS signal with a maximum strength of 14000 cnts at 1072 cm⁻¹ (curve a in Fig.4C). Hence, the Es can also be estimated that the enhancement effect of 532 nm is ~20 times that of 785 nm on ML-Ag (Fig.4D). These relative comparisons indicated that the presence of UC materials improved nearly one order of magnitude of the SERS enhancement under excitation laser of 785 nm.



Figure 4. (A) The SERS spectra of 10^{-6} M pATP on UC@Ag under (a) 532nm, (b) 785nm; (B) The comparison of enhancement effects of the two excitation lasers. (C) The SERS spectra of 10^{-6} M pATP on ML-Ag under (a) 532nm, (b) 785nm; (D) The comparison of enhancement effects of the two excitation lasers.

Particularly, an enhancement in the SERS intensities is expected if there is an increase in the number of adsorbed analyte molecules on the UC@Ag than the ML-Ag substrate in a given cross-section. However, this possibility may be ruled out by examining the relative variations of peak intensities in a plasmon-driven chemical reaction. Recently, many research results clearly demonstrated the promising potential of surface plasmon used as a novel "catalytic" media to understand possible chemical reactions induced by laser excitation.^{28, 29}



Figure 5. (A) Time-dependent SERS spectra of pNTP under continuous exposure to a 785 nm laser. The spectra were collected on UC@ Ag particles, with an integration time of 2 s. (B and C) Illumination time-dependent Raman intensities of the peaks at 1335, 1143 and 1440 cm⁻¹, respectively. (D) Illumination timedependent relative Raman intensities of 1143 and 1440 cm⁻¹ peaks normalized by the intensities of the 1335 cm⁻¹ peak.

In the context described above, the plasmonic photocatalysis of pNTP dimerizing into DMAB was investigated on single particle of UC@Ag and the ML-Ag substrate, respectively. A time-course SERS mapping was performed on a single-particle of UC@Ag under continuous exposure to a 785 nm laser (Fig. 5). As the exposure time increased, the SERS intensity of v(NO₂) stretching mode at 1335 cm⁻¹ decreased dramatically (Fig.5A and B). The peaks at 1385 and 1440 cm⁻¹ which are attributed to the v(N=N) stretching mode and 1143 cm⁻¹ which is attributed to the β (CH) stretching mode of DMAB gradually increased (Fig.5C), which cannot be observed in normal Raman spectrum (Fig.S7).²⁸ This alteration indicated the dimerizing of pNTP molecules into DMAB. It is worth mentioning that the intensities of v(N=N) and $\beta(CH)$ slightly decreased after about 500 s exposure (Fig.5C). The whole measuring process lasted more than 10 mins, therefore, long time exposure may cause the signal attenuation and local structure alteration of the substrate. Fig.5D shows the illumination time dependence of the relative intensities of the 1143 and 1440 cm⁻¹ peaks normalized by the 1335 cm⁻¹ peak, according to the equation: $\Delta_i = I_i/I_{1335}$, I is the value of peak intensity. The ratio (Δ_{1440}) can represent the apparent conversion rate of pNTP into DMAB to some extent.

2

3

4

5

6

7

8

9

10

11

12

13

14 15

16

17

18 19

20

21

22

23

24

25

26

27

28

29

30

Journal Name

Analyst



Figure 6. The Δ_{1440} curves under continuous exposure to the lasers of 532 nm and 785 nm on UC@Ag (A and B) and ML-Ag (C and D), respectively. The error bars represent standard deviation in triplicated experiments.

Similarly, a time-course SERS mapping was also performed on single-particles of UC@Ag under continuous exposure to a 532 nm laser under similar conditions (Fig.S8). The Δ_{1440} under the laser of 532 nm reached a relatively stable value of about 1.1 after about 300 s illumination, and the laser of 785 nm made a smaller value of about 0.8 (Fig. 6B). The error bars represent the standard deviation of the apparent conversion rate obtained with three sets of time-course SERS mappings. It can be estimated that the Δ_{1440} of 532 nm is only ~1.38 times that of 785 nm on the UC@Ag particles. To corroborate the enhanced photocatalysis on UC@Ag, the plasmon-driven photocatalysis was also investigated on the ML-Ag substrate under the excitation lasers of 532 nm and 785 nm, respectively. Fig. 6C illustrated that the stable Δ_{1440} excited by the 532 nm laser is about 0.75 and that by the 785 nm laser is only about 0.1. Hence, it can also be estimated that the Δ_{1440} of 532 nm is ~7.5 times of that of 785 nm on ML-Ag substrate (Fig. 6D). The ratios of the apparent conversion rate on the same substrate eliminate the concentration effect of the adsorbed molecules and other negative effects.

$\frac{\text{MR}hr}{\text{Vb}^{3}} = E^{3}$ $\frac{\text{MR}hr}{\text{R}hr}$ $\frac{\text{Hot electrons}^{*}}{\text{Hot electrons}^{*}}$ $\frac{\text{Hot electrons}^{*}}$

Scheme 2. Schematic illustration of the plasmon-driven chemical reaction of pNTP dimerizing into DMAB on UC@Ag.

It is worth speculating on the origin of difference in Raman enhancment and conversion rate in photocatalysis between UC@Ag and ML-Ag. The presence of UC materials might provide more excitation lines and much stronger plasmon resonance. The stronger LSPR produce higher density of "hot"

electrons which can boost the chemical reaction (Scheme 2). Furthermore, the "hot" electrons with high kinetic energy above the Fermi level could jump to the unoccupied resonant energy level of chemical reactants near the metal surface and transfer to the intra- molecular vibrational energy during the interactions.³⁰ In both cases the energy barrier of the chemical reactions could be reduced.³¹ So far, we conclude that UC serve as a light converter to upconvert the NIR light into the visible one, the highly plasmon resonance will be induced because the LSPR of Ag NPs appears in the visible spectral range. In addition, the energy transfer from excited Yb³⁺ to Er³⁺ in UC will enhance the local field density which can induce the plasmon field enhancement effect, both of the effects will act on the SERS performance, resulting in the significantly improved Raman enhancement and plasmon photocatalytic ability.

Conclusions

The UC material was successfully incorporated into the SERSactive substrates for the first time. It has demonstrated that the NIR laser with low power can also obtain the excellent signals on UC@Ag in comparison with the conventional SERS measurements on pure Ag substrates. Moreover, the electrons transition in UC particles produced strong plasmon resonances which can boost the chemical reaction, also the perfect plasmon photocatalytic ability was obtained under the NIR excitation with a relatively low laser power. The NIR excitation for the UC@Ag substrate provided a deeper penetration depth and a low power, opening up a new application field of UC-noble metal composite, especially for biological application. Furthermore, it also promises a new research direction for the synthesis and applications of SERS-active nanostructures.

Acknowledgements

This work was supported by the National Basic Research Program of China (2011CB933700), the National Instrumentation Program of China (2011YQ0301241001 & 2011YQ0301241101), National Natural Science Foundation of China (21305142, 61273066 and 11205204), and Natural Science Foundation of Anhui Province, China (1308085QB27). **Notes and references**

Corresponding Author

* Phone: +86-551-6559-2385. Fax: +86-551-6559-2420. E-mail: hlliu@iim.ac.cn, lbyang@iim.ac.cn.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

- H. L. Liu, Z. L. Yang, L. Y. Meng, Y. D. Sun, J. Wang, L. B. Yang, J. H. Liu and Z. Q. Tian, *J. Am. Chem. Soc.*, 2014, **136**, 5332-5341.
- 2. J. A. Dougan and K. Faulds, Analyst, 2012, 137, 545-554.
- J. F. Li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fan, W. Zhang, Z. Y. Zhou, D. Y. Wu, B. Ren, Z. L. Wang and Z. Q. Tian, *Nature*, 2010, **464**, 392-395.
- W. Xie, C. Herrmann, K. Kompe, M. Haase and S. Schlucker, J. Am. Chem. Soc., 2011, 133, 19302-19305.

2

3

4

5

6

7

8

9

10

11

12

13

14 15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47 48

49

50 51

53

54

55

56

57

58

59 60

- M. Grabiec, A. Wolak, O. Veron, J. P. Blondeau, N. Pellerin, M. Allix, S. Pellerin and K. Dzierzega, *Plasmonics*, 2012, 7, 279-286.
- Y. M. Ma, H. L. Liu, K. Qian, L. B. Yang and J. H. Liu, J. Colloid Interf. Sci., 2012, 386, 451-455.
- Y. W. Zhang, S. Liu, L. Wang, X. Y. Qin, J. Q. Tian, W. B. Lu, G. H. Chang and X. P. Sun, *Rsc Adv.*, 2012, 2, 538-545.
- A. D. McFarland, M. A. Young, J. A. Dieringer and R. P. Van Duyne, J. Phys. Chem. B, 2005, 109, 11279-11285.
- J. Zhao, J. A. Dieringer, X. Y. Zhang, G. C. Schatz and R. P. Van Duyne, J. Phys. Chem. C, 2008, 112, 19302-19310.
- 10. Y. M. Ma, Q. Q. Ding, L. B. Yang, L. Zhang and Y. H. Shen, *Appl. Surf. Sci.*, 2013, 265, 346-351.
- 11. H. L. Liu, Y. D. Sun, Z. Jin, L. B. Yang and J. H. Liu, *Chem. Sci.*, 2013, **4**, 3490-3496.
- 12.B. Crisan, O. Soritau, M. Baciut, R. Campian, L. Crisan and G. Baciut, *Particul. Sci. Technol.*, 2013, **31**, 168-173.
- 13. A. Lee, G. F. S. Andrade, A. Ahmed, M. L. Souza, N. Coombs, E. Tumarkin, K. Liu, R. Gordon, A. G. Brolo and E. Kumacheva, *J. Am. Chem. Soc.*, 2011, **133**, 7563-7570.
- 14. H. C. Jeon, C. J. Heo, S. Y. Lee and S. M. Yang, Adv. Funct. Mater., 2012, 22, 4268-4274.
- 15. F. Wang, Y. Han, C. S. Lim, Y. H. Lu, J. Wang, J. Xu, H. Y. Chen, C. Zhang, M. H. Hong and X. G. Liu, *Nature*, 2010, **463**, 1061-1065.
- 16. F. Wang, D. Banerjee, Y. S. Liu, X. Y. Chen and X. G. Liu, *Analyst*, 2010, **135**, 1839-1854.
- J. C. Goldschmidt, S. Fischer, H. Steinkemper, F. Hallermann, G. von Plessen, K. W. Kramer, D. Biner and M. Hermle, *Ieee J. Photovolt.*, 2012, 2, 134-140.
- W. Feng, L. D. Sun and C. H. Yan, *Chem. Commun.*, 2009, 4393-4395.
- S. Schietinger, T. Aichele, H. Q. Wang, T. Nann and O. Benson, *Nano Lett.*, 2010, **10**, 134-138.
- 20. H. P. Paudel, L. L. Zhong, K. Bayat, M. F. Baroughi, S. Smith, C. K. Lin, C. Y. Jiang, M. T. Berry and P. S. May, *J. Phys. Chem. C*, 2011, 115, 19028-19036.
- J. H. Wu, J. L. Wang, J. M. Lin, Z. Lan, Q. W. Tang, M. L. Huang, Y. F. Huang, L. Q. Fan, Q. B. Li and Z. Y. Tang, *Adv. Energy. Mater.*, 2012, 2, 78-81.
- 22. T. Jiang, Y. Liu, S. S. Liu, N. Liu and W. P. Qin, J. Colloid Interf. Sci., 2012, 377, 81-87.
- 23. N. Liu, W. P. Qin, G. S. Qin, T. Jiang and D. Zhao, *Chem. Commun.*, 2011, **47**, 7671-7673.
- 24.M. Rycenga, C. M. Cobley, J. Zeng, W. Y. Li, C. H. Moran, Q. Zhang, D. Qin and Y. N. Xia, *Chem. Rev.*, 2011, **111**, 3669-3712.
- 25. S. M. Stranahan, E. J. Titus and K. A. Willets, Acs Nano, 2012, 6, 1806-1813.
- 26. H. L. Liu, L. B. Yang, H. W. Ma, Z. M. Qi and J. H. Liu, *Chem. Commun.*, 2011, 47, 9360-9362.
- 51 27. B. H. Liu, G. M. Han, Z. P. Zhang, R. Y. Liu, C. L. Jiang, S. H. Wang
 52 and M. Y. Han, *Anal. Chem.*, 2012, 84, 255-261.
 - 28. L. L. Kang, P. Xu, B. Zhang, H. H. Tsai, X. J. Han and H. L. Wang, *Chem. Commun.*, 2013, **49**, 3389-3391.
 - 29.B. Dong, Y. R. Fang, X. W. Chen, H. X. Xu and M. T. Sun, *Langmuir*, 2011, **27**, 10677-10682.
 - J. Yang, D. Wang, H. Han and C. Li, *Accounts Chem. Res.*, 2013, 46, 1900-1909.

31. M. T. Sun, Z. L. Zhang, H. R. Zheng and H. X. Xu, Sci. Rep., 2012, 2, 647(1-4).

Analyst

6 | J. Name., 2012, 00, 1-3



NaYF₄:Yb,Er

Upconversion material-noble metal composites initiate greatly improved Raman scattering and plasmon photocatalysis, promising a novel direction for fabricating SERS-active nanostructures.