Т. 86, № 2 **ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ** МАРТ — АПРЕЛЬ 2019
V. 86, N 2 **JOURNAL OF APPLIED SPECTROSCOPY** MARCH — APRIL 2019

# SURFACE-ENHANCED RAMAN SCATTERING SPECTROSCOPY AS AN ON-SITE RAPID MEASUREMENT TOOL FOR DETECTION OF EXPLOSIVES[**]

**Maosheng Yu, Junsheng Wang, Junqing Chen, Jingjing Hou, Fengli Bei** [*]

*Key Laboratory for Soft Chemistry and Functional Materials,*
*Nanjing University of Science and Technology, Ministry of Education, Nanjing 210094, P. R. China;*
*National Quality Supervision and Inspection Center for Industrial Explosive Materials,*
*Nanjing, 210094, P. R. China; e-mail: beifl@njust.edu.cn*

*Detection of explosives, especially on-site rapid detection of trace amount of explosives, is of great concern for homeland security and environmental issues. Surface-enhanced Raman Scattering (SERS) spectroscopy is demonstrated to enable high sensitivity to detect trace explosives levels. Herein we have assembled silver nanoparticles (AgNPs) on normal glass slides (GS) to form a novel SERS substrate. It is noteworthy that this substrate realizes the regulation of hot spots and its uniform distribution. By using this substrate, cyclotetramethylenetetranitramine (HMX) has been successfully measured to as low as* $3\times10^{-8}$ *M. Moreover this SERS substrate can also be employed in the detection of other explosives, such as cyclotrimethylenetrinitramine (RDX) and trinitrotoluene (TNT). The advantages including low cost, ultra-high sensitivity, and facile manipulation of the sample preparation make the SERS spectroscopy a rapid and powerful on-site instrument in trace detection of explosives.*

***Keywords:*** *SERS, on-site rapid detection, explosives.*

# СПЕКТРОСКОПИЯ ГИГАНТСКОГО КОМБИНАЦИОННОГО РАССЕЯНИЯ КАК СРЕДСТВО ДЛЯ ОПЕРАТИВНОГО ОБНАРУЖЕНИЯ ВЗРЫВЧАТЫХ ВЕЩЕСТВ

**M. Yu, J. Wang, J. Chen, J. Hou, F. Bei**[*]

*УДК 535.375.5;541.427.6*

*Нанкинский университет науки и техники, Нанкин,*
*210094, Китай; e-mail: beifl@njust.edu.cn*
*Национальный центр по надзору и контролю качества промышленных взрывчатых материалов,*
*Нанкин, 210094, Китай*

*(Поступила 2 мая 2018)*

*Для обнаружения взрывчатых веществ на следовом уровне с помощью спектроскопии гигантского комбинационного рассеяния (ГКР) путем сборки наночастиц серебра на обычных стеклянных предметных стеклах сформирована подложка для ГКР. Созданная подложка позволяет осуществлять регулирование горячих точек и их равномерное распределение. С этой подложкой измерено содержание циклотетраметилентетранитрамина, не превышающее* $3\times10^{-8}$ *М. Такая подложка для ГКР может также использоваться для обнаружения других взрывчатых веществ, таких как циклотриметилентринитрамин и тринитротолуол.*

***Ключевые слова:*** *гигантское комбинационное рассеяние, оперативное обнаружение, взрывчатые вещества.*

---

[**] Full text is published in electronic version of ZhPS V. 86, No. 2 (http://www.elibrary.ru/title_about.asp?id=7318; sales@elibrary.ru).

**Introduction.** Developing techniques like rapid and accurate detection of various explosives is an urgent problem for homeland security, in particular after the “9.11” terrorist attacks [1]. Corresponding techniques such as terahertz spectroscopy [2, 3], mass spectrometry [4, 5], bio-chemical sensors [6–8], electrochemical sensors [9, 10], and so on have been well developed. However shortages like the high cost, large sizes, and unfriendly operating systems hinder their widespread applications, especially for an on-site detection.

Fortunately Raman spectroscopy, a powerful “chemical fingerprint” technology, provides a new perspective on this field. Its superior properties, including the convenient sample preparation, “non-contract” detection, and good portability, render it wellsuited for on-site measurements, but the low cross section of Raman scattering has greatly hampered its detection limits. The recently developed surface enhanced Raman scattering (SERS), which can achieve enhancement of Raman signals by several orders of magnitude, if the target molecules are adsorbed properly on roughened surfaces of some metal substrates, has revitalized this approach [11, 12]. As a result, the application area of Raman spectroscopy has been extended significantly, even making its sensitivity high enough to support on-site detection for sample in trace amount.

Up to now, this technique has been utilized to detect explosives [13, 14]. Earlier, taking into account of the high sensitivity of SERS for aromatic ring type structures, it has been used to detect the nitroaromatics. Kneipp et. al. demonstrated that a detection limit of $1\times10^{-7}$ M can be obtained for trinitrotoluene (TNT) by using aggregated colloidal gold in aqueous solution [15]. Later on, significant progress was achieved by S. R. Samuel with coworkers, who had lowered the detection limit to as low as $2\times10^{-12}$ M. Their success depended critically on a brand new designed substrate, in which cysteine is used as a “linker” to connect gold on gold nanoparticles and target molecules such as TNT in this case into one body to form a Meisenheimer complex [16]. The electrostatic interaction between gold nanoparticle bound Meisenheimer complex and cysteine bound gold nanoparticle induces the aggregation of nanoparticles, which thus greatly enhance the detection efficiency. Ben-Jaber et. al. demonstrated that silver nanocubes (AgNCs) were developed as a highly sensitive SERS substrate with very low limit of detection (LOD) for explosive materials down to the femtomolar ($10^{-15}$ M) range [17]. Besides, the detection of nitramine compounds such as cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) has also drawn great attention. Specifically, RDX and HMX can be measured at $4\times10^{-4}$ M by SERS using gold coated substrate produced by nanospheres imprint technique [18]. While Hatab et al. even reported a measurement of RDX up to $1\times10^{-6}$ M for a contaminated ground water. It should be mentioned that this work is the first example to extend the SERS to environmental science [19].

To be an on-site technique of high performance, SERS spectroscopy requires high sensitivity and reliability, and easy-operating. While SERS has demonstrated its great promise in the detection of explosives, all current systems have their inherent problems. For systems with unmodified substrates (without linker groups), they are encumbered by the limited sensitivity. On the other hand, for systems with “linker” modified ones, they can only detect one specific explosive while a wide spectrum detection of explosives with various structures cannot be supported. Hence the design, control and fabrication of substrates with well-defined structures have become a great issue in this field.

For this purpose, we have fabricated arrays of silver nanoparticles (AgNPs) as a SERS substrate whose structure is that poly (diallyldimethylammonium chloride) (PDDA) as an intermediate to allow AgNPs to be absorbed on the hydroxylated glass slides by electrostatic interactions. One significant advantage for this substrate is its capability to realize the density control and uniform distribution of “hot” spots facilely by controlling the immersion time of the modified glass slides in silver colloids. It is believed that hot spots occur in the gaps between adjacent metallic nanostructures, where extremely intense local electromagnetic fields upon optical excitation [20]. Some obvious studies have shown that largest SERS enhancement did not occur for the smallest gaps [21]. As long as the analytic molecules absorbed within the gaps (in sub 10 nm range), it would achieve large SERS enhancement [22, 23]. On this basis, we believe deposition of the explosives directly on substrates physically can in theory achieve the same target. Hence in this paper, the explosives are deposited on substrates physically by dropping a fixed volume of the explosive solutions on the surface until the solvent is evaporated completely. One typical feature for this method is the lack of using a chemical linker, which greatly simplifies the sample preparation dramatically. Due to this, the method can be even extended to an on-site rapid detection. To evaluate the sensitivity and universality of the substrate, HMX, RDX, and TNT are used as our sample compounds. High quality Raman spectra of these compounds are obtained and compared with their corresponding counterparts in bulk. In addition, the influence of soaking time for the modified glass slide submerged in silver colloids and the detection limit of HMX have been studied.

**Experiment.** HMX, RDX, and TNT are obtained from National Quality Supervision and Inspection Center for Industrial Explosive Materials. PDDA is purchased from Aldrich. $AgNO_3$ is obtained from Shanghai Chemical Reagent. Sodium citrate, acetone, ethanol, $H_2O_2$, and $H_2SO_4$ all are purchased from Sinopharm Chemical Reagent Co., Ltd. Water used throughout the operation is distilled through Millipore water purification system with a resistivity of 18.2 MΩ.

The Raman spectra are recorded on a Renishaw Micro-Raman spectroscopy. The excitation line at 785 nm provided by an emitting laser diode is used. The morphologies of the prepared silver colloids and substrates are observed by TEM (JEM-2100, 200 kV) and SEM (S4800, 30 kV), respectively.

The synthesis of metal nanoparticles follows through the mature procedures. In this work, the silver colloids are prepared according to the work reported by P. C. Lee and D. Meisel [24]. Specifically, $AgNO_3$ (45 mg) is dissolved in 250 mL of $H_2O$ and heated to boiling state. Then a solution of sodium citrate (4.5 mL, ms 1%) is added in drop-wise. The mixture is kept boiling for 1 h.

Figure 1 describes the basic strategy for the assembly of silver nanospheres on the modified glass slides. At first, 5×5 mm glass slides were pre-treated by the mixed solution of $H_2SO_4$ and $H_2O_2$ (with a volume ratio of 1:3) for 8 h, and then the slides were rinsed with water. Subsequently, the above clean slides were immerged in PDDA (1% in water) for 8 h. After that, PDDA was washed out from the modified glass slides by water thoroughly. Finally, the modified glass slides were submerged in silver suspension for 3.5 h, and then the substrate were rinsed with extensive water and dried in dark place.

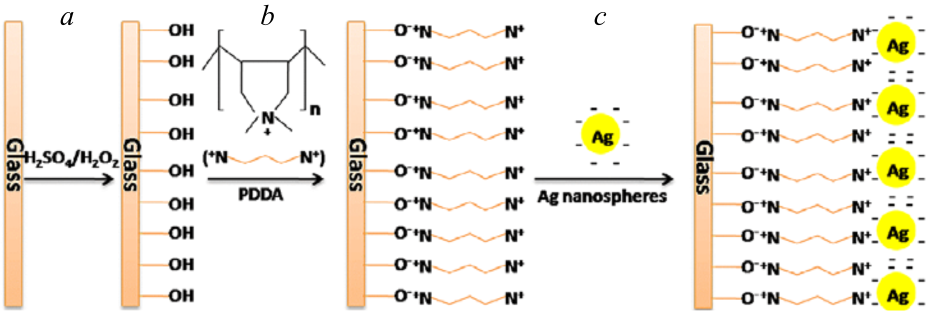

Fig. 1. Schematic description of the three-step procedures for the assembly of the substrates: reactive silanol groups that were generated on the glass surface by rinsing with $H_2SO_4/H_2O_2$ solution (a), the exposed silanol groups on glass slide surface were reacted with electropositive nitrogen of PDDA by electrostatic interactions to produce anchor sites for silver nanoparticles (b), the terminal ammonium groups of PDDA react with the electronegative silver nanospheres to generate the final substrate (c).

**Results and discussion.** The TEM images of the AgNPs obtained are shown in Fig. 2a, in which the AgNPs show a relatively similar distribution with an average diameter of 70 nm. The SEM images of SERS substrates are shown in Fig. 2b–d. As can be observed, AgNPs have been adsorbed on the derived glass slides. Because of the different soaking time of the derived glass slide submerged in Ag colloids, the amount of the absorption is various. In Fig. 2b, only 1 h of the derived glass slide is immersed in Ag colloids, so only relatively few AgNPs and large interparticle gaps are observed. With an increase of the soaking time to 3.5 h (Fig. 2c), the absorbing capacity of AgNPs becomes larger and AgNPs are aggregated, superior for the formation of hot spots. Upon soaking time to an even long time, say 6 h in Fig. 2d, a lot of AgNPs aggregate together and could induce over aggregation. Nevertheless, the latter may be harmful for SERS signal generation. In order to demonstrate our hypothesis, the SERS spectra of HMX are varied as a function of soaking time of the derived glass slides. Figure 2e shows the recorded spectra of $3\times10^{-7}$ M HMX on the SERS substrates with a soaking time of 1.0, 3.5, and 6.0 h. It can be seen that a steady increase of SERS signal for substrates soaking at a longer time, meanwhile lots of peaks disappear even though the intensity of some few peaks are enhanced. Thus, aggregation is benefit for the formation of the SERS hot spots. Excess soak time leads to unfavorable adsorption of AgNPs and causes over aggregation of the system which results in a drop of Raman signals. By controlling the soaking time, we can control the hot spots both in distribution and the density. In summary, this method can realize the regulation and optimization of hot spots, which is important for on-site rapid detection. The measuring SERS spectrum of HMX is shown in Fig. 2f (curve 1). To eliminate the influence of SERS substrate, another measurement for AgNPs/GS is performed, and the spectrum is shown in Fig. 2f (curve 2). For comparison, normal Raman spectrum of HMX in bulk state is shown in

Fig. 2f (curve 3). The corresponding peaks are assigned in Table. 1. It can be seen clearly that the corresponding signal intensities are much higher if the substrate is used. It should be mentioned that this kind of substrate has advantages of facile preparation, easy operation and excellent sensitivity, which makes it superior in the measurement and potentially a good candidate for on-site rapid detection of explosives in practice.

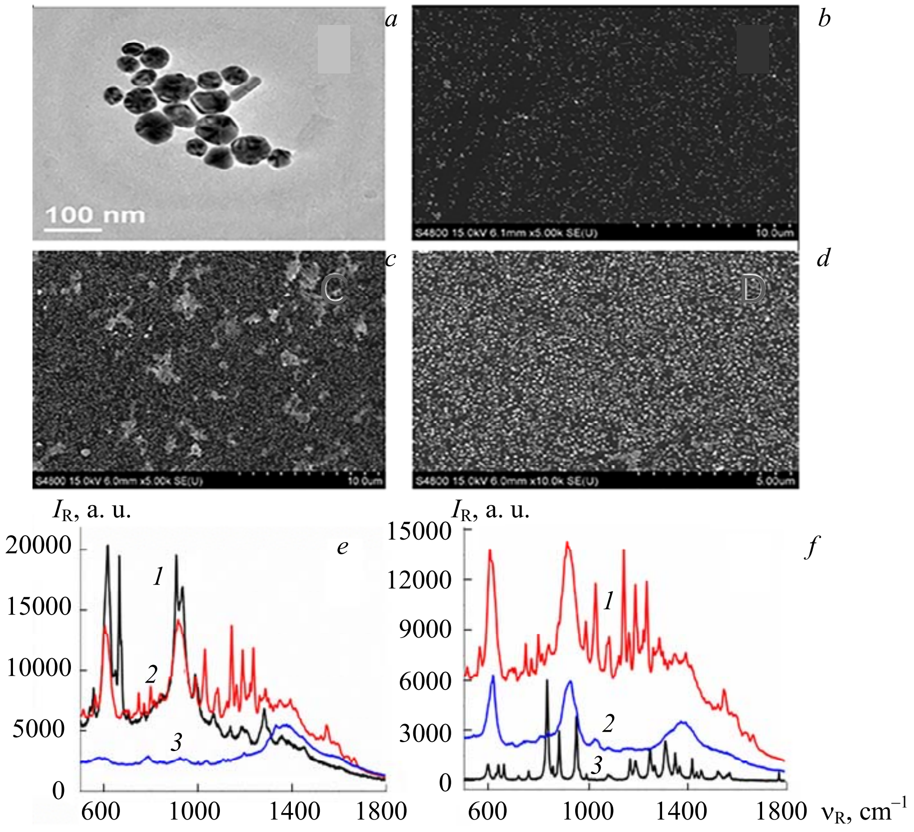

Fig. 2. TEM image of Ag nanospheres (a); SEM image of the modified glass slide that was submerged into Ag colloids for 1 (b), 3.5 (c), 6 h (d); SERS spectra of $3.4\times10^{-7}$ MHMX on SERS substrates with different soaking time of the modified slides submerged in Ag colloids (e): 6 (1), 3.5 (2), 1 h (3). (f): SERS spectra of $3\times10^{-7}$ M HMX (1), Raman spectra of AgNPs/GS substrate (2), and Raman spectra of bulk HMX (3).

TABLE 1. References [25, 26] and Experimental Raman Shift (cm$^{-1}$) and Band Assignments for HMX

| Assignment | Solid [25, 26] | Experiment | |
|---|---|---|---|
| | | Solid | SERS substrates |
| $\beta$(NNO) | 597 | 597 | 603 |
| $\beta$(NNO),$\upsilon$(NN) | 638 | 638 | |
| $\beta$(NNO),$\upsilon$(NN) | 662 | 660 | 662 |
| $\beta$(ONO),$\upsilon$(CN) | 721 | 720 | 746 |
| $\sigma$(ONO) | 762 | 760 | 770 |
| $\upsilon_s(NC_2)$ | 834 | 835 | 840 |
| $\upsilon_s(NNC_2)$ | 884 | 883 | 906 |
| $\upsilon$(NN),$\rho(CH_2)$ | 953 | 953 | 988 |
| $\upsilon_{as}(NNC_2)$ | 1080 | 1078 | 1084 |
| $\upsilon_{as}$(CNN),$\rho(CH_2)$ | 1168 | 1168 | 1164 |
| $\upsilon_{as}(NC_2)$ | 1192 | 1191 | 1190 |
| $\upsilon_{as}(NC_2)$ | 1248 | 1251 | 1237 |
| $\upsilon_s(NO_2)$ | 1268 | 1267 | 1263 |
| $\gamma(CH_2)$ | 1312 | 1311 | 1332 |

*Continue Table 1*

| Assignment | Solid [25, 26] | Experiment | |
|---|---|---|---|
| | | Solid | SERS substrates |
| $\gamma(CH_2)$ | 1351 | 1350 | 1349 |
| $\omega(CH_2)$ | 1369 | 1368 | 1394 |
| $\omega(CH_2)$ | 1418 | 1420 | |
| $\beta(HCH)$ | 1438 | 1438 | |
| $\beta(HCH)$ | 1460 | 1455 | |
| $\upsilon_{as}(NO_2)$ | 1532 | 1527 | 1523 |
| $\upsilon_{as}(NO_2)$ | 1558 | 1558 | 1548 |
| $\upsilon_{as}(NO_2)$ | | 1569 | |

Note. $\beta(XYZ)$: bend of X–Y–Z angle; $\gamma(XY_2)$: twist about bisector of Y–X–Y angle; $\omega(XY_2)$: wag of $Y_2$ atoms out of $XY_2$ plane; $\sigma(XY_2)$: wag of X atom out of $XY_2$ plane; $\rho(XY_2)$: rocking in $XY_2$ plane; $\upsilon(XX)/\upsilon(XY)$: stretch of X–X or X–Y bonds; $\upsilon_s(XY_2)$: symmetric stretch of Y–X–Y bonds; $\upsilon_s(XXY_2)$: symmetric stretch of X–X–$Y_2$ bonds; $\upsilon_{as}(XY_2)$: asymmetric stretch of Y–X–Y bonds.

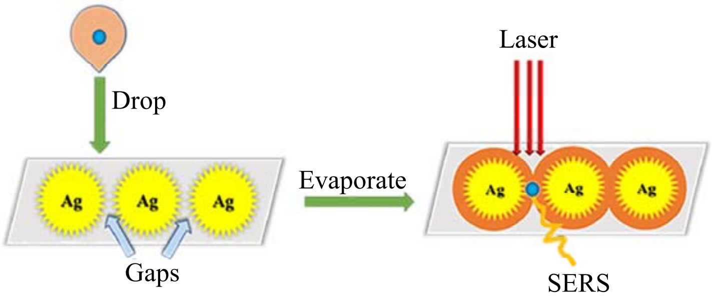

Fig. 3. Schematic of the process and mechanism of detection.

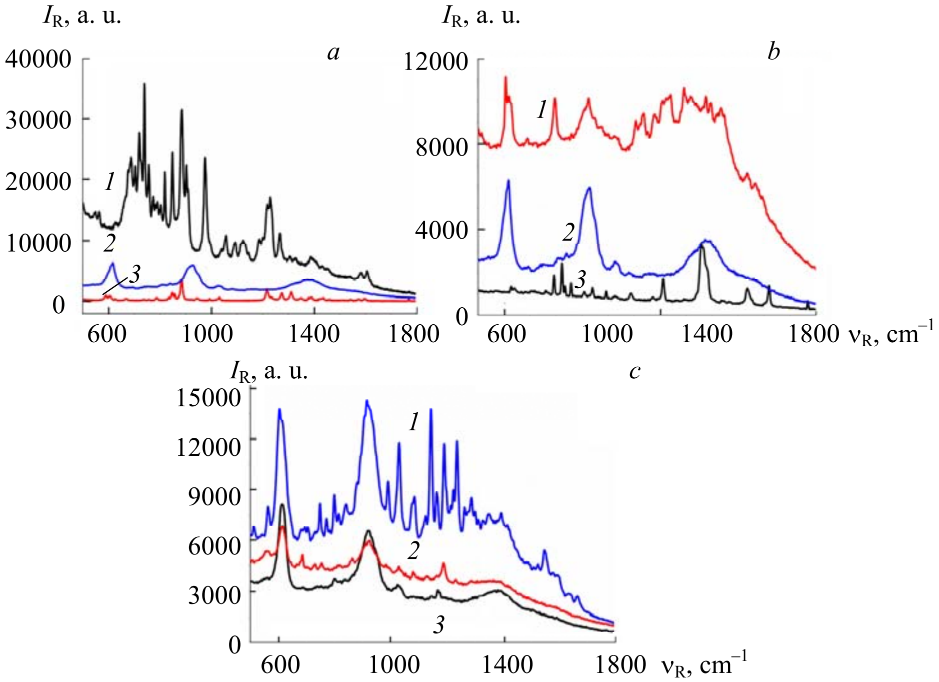

Fig. 4. SERS spectra (a) of $4\times10^{-7}$ M RDX (1), Raman spectra of AgNPs/GS substrates (2), Raman spectra of bulk RDX (3). SERS spectra (b) of $4\times10^{-7}$ M TNT (1), Raman spectra of AgNPs/GS substrates (2), Raman spectra of bulk TNT (3). SERS spectra of HMX with concentrations $3\times10^{-7}$ (1), $1.5\times10^{-7}$ (2), $3\times10^{-8}$ M (3) on the SERS substrates, laser power ~2 mW and the scan time ~10 s (c).

Figure 3 shows the schematic of the process and the mechanism of detection. In this study, the desired explosive molecule is absorbed on the substrate by simple dropping a volume of the corresponding solution on the surface of the substrate until the solvent evaporates completely. Based on the results from TEM and SEM studies, the hot spots of this kind of substrate are in an array of uniform distribution. We believe such high activity can be attributed to the increased possibility for target molecules to be located within the AgNPs upon solvent evaporation. This will enhance the chances to generate hot spots in the measurement.

We try to clarify whether the SERS substrates fabricated here can be extended to other common small organic explosive molecules or not, and therefore RDX and TNT are selected as the substrate molecules. RDX belongs to the family of HMX as one commonly used explosive. TNT is a leading example of nitroaromatic explosive. Figures 4a,b show the SERS spectra of $4\times10^{-7}$ M RDX and TNT molecule obtained from the SERS substrates. The main vibrational modes for the analysis of RDX and TNT are clearly displayed and well separated from SERS substrates Raman bonds. The intensity of SERS spectra is stronger than normal Raman spectra of bulk RDX and TNT under same test environment. It is demonstrated that the SERS spectra of RDX and TNT is still identifiable even at a concentration of $4\times10^{-7}$ M, which enables SERS-based ultra-sensitive detection of RDX and TNT to be an on-site rapid measuring tool. To verify the sensitivity of our SERS probe, different concentrations of HMX acetonitrile aqueous solution are evaluated. Figure 4c shows the SERS spectra of different concentrations of HMX acetonitrile aqueous solution, which is dropped on the surface of AgNPs/GS substrates. Our experimental results demonstrate clearly that the detection capability of the method can be as low as $3\times10^{-8}$ M for HMX and still show enhanced Raman peaks.

**Conclusion.** This study has presented a cheap and easy approach to fabricate AgNPs/GS substrates. As an active substrate, this SERS substrate exhibits excellent enhancement ability for a wide family of explosives such as HMX, RDX, and TNT. The soak time of the derived slides submerged into Ag colloids plays an important role in the determination of SERS sensitivities. By controlling the soak time of the derived slides submerged into Ag colloids, the amount and the distribution of the hot spots produced on the substrates could be able to be optimized. In addition, the concentration of HMX could be detected as low as $3\times10^{-8}$ M using the SERS substrates fabricated. This study will be helpful in trace detection for explosives using SERS spectroscopy as an on-site rapid measuring tool.

**Acknowledgment.** This work is partially supported by the National Natural Science Foundation of China (51472119 and 21474053). A project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

## REFERENCES

1. Z. H. Xu, J. M. Hao, W. Braida, D. Strickland, F. S. Li, X. G. Meng, *Langmuir*, **27**, No. 22, 13773–13779 (2011).
2. E. M. Witko, W. D. Buchanan, T. M. Korter, *J. Phys. Chem. A*, **115**, No. 44, 12410–12418 (2011).
3. M. R. Leahy-Hoppa, M. J. Fitch, X. Zheng, L. M. Hayden, R. Osiander, *Chem. Phys. Lett.*, **434**, No. 4-6, 227–230 (2007).
4. X. P. Pan, K. Tian, L. E. Jones, G. P. Cobb, *Talanta*, **70**, No. 2, 455–459 (2006).
5. J. J. Brady, E. J. Judge, R. J. Levis, *Rapid Commun. Mass Spectrom.*, **24**, No. 11, 1659–1664 (2010) .
6. A. A. Adams, P. T. Charles, J. R. Deschamps, A. W. Kusterbeck, *Anal. Chem.*, **83**, No. 22, 8411–8419 (2011).
7. N. Cennamo, G. D'Agostino, R. Galatus, L. Bibbo, M. Pesavento, L. Zeni, *Sens. Actuators, B*, **188**, 221–226 (2013).
8. A. Gingras, J. Sarette, E. Shawler, T. Lee, S. Freund, E. Holwitt, B. W. Hicks, *Biosens. Bioelectron.*, **48**, 251–257 (2013).
9. H. X. Zhang, A. M. Cao, J. S. Hu, L. J. Wan, S. T. Lee, *Anal. Chem.*, **78**, No. 6, 1967–1971 (2006).
10. A. M. O'Mahony, J. Wang, *Anal. Methods*, **5**, No. 7, 4296–4309 (2013).
11. P. H. B. Aoki, L. N. Furini, P. Alessio, A. E. Aliaga, C. J. L. Constantino, *Rev. Anal. Chem.*, **32**, No. 1, 55–76 (2013).
12. S. Botti, L. Cantarini, A. Palucci, *J. Raman Spectrosc.*, **41**, No. 8, 866–869 (2010).
13. I. Talian, J. Huebner, *J. Raman Spectrosc.*, **44**, No. 4, 536–539 (2013).
14. J. Y. Xu, J. Wang, L. T. Kong, G. C. Zheng, Z. Guo, J. H. Liu, *J. Raman Spectrosc.*, **42**, No. 9, 1728–1735 (2011).

15. K. Kneipp, Y. Wang, R. R. Dasari, M. S. Feld, B. D. Gilbert, J. Janni, J. I. Steinfeld, *Spectrochim. Acta, A*, **51**, No. 12, 2171–2175 (1995).
16. S. S. R. Dasary, A. K. Singh, D. Senapati, H. T. Yu, P. C. Ray, *J. Am. Chem. Soc.*, **131**, No. 38, 13806–13812 (2009) .
17. S. Ben-Jaber, W. J. Peveler, R. Quesada-Cabrera, C. W. O. Sol, I. Papakonstantinou, I. P. Parkin, *R. Soc. Chem.*, **9**, 16459–16466 (2017).
18. F. A. Calzzani Jr., R. Sileshia, A. Kassu, J. M. Taguenang, A. Chowdhury, A. Sharma, P. B. Ruffin, C. Brantley, E. Edwards, *Proc. Soc. Photo-Opt. Instrum. Eng.*, **6945**, 69451O-1-69451O-9 (2008).
19. N. A. Hatab, G. Eres, P. B. Hatzinger, B. H. Gu, *J. Raman Spectrosc.*, **41**, No. 10, 1131–1136 (2010).
20. S. Lal, N. K. Grady, J. Kundu, C. S. Levin, J. B. Lassiterde, N. J. Halas., *Chem. Soc. Rev.*, **37**, No. 5, 898–911 (2008).
21. L. D. Qin, S. L. Zou, C. Xue, A. Atkinson, G. C. Schatz, C. A. Mirkin, *Proc. Natl. Acad. Sci. USA*, **103**, No. 36, 13300–13303 (2006).
22. H. Wang, C. S. Levin, N. J. Halas, *J. Am. Chem. Soc.*, **127**, No. 43, 14992–14993 (2005).
23. D. K. Lim, K. S. Jeon, H. M. Kim, J. M. Nam, Y. D. Suh, *Nat. Mater.*, **9**, No. 1, 60–67 (2010).
24. P. C. Lee, D. Meise, *J. Phys. Chem.*, **86**, No. 17, 3391–3395 (1982).
25. K. D. Zoha, M. K. Stenstrom, *Water Res.*, **36**, No. 5, 1331 (2002).
26. H. V. Brand, R. L. Rabie, D. J. Funk, I. Diaz-Acosta, P. Pulay, T. K. Lippert, *J. Phys. Chem. B*, **106**, No. 41, 10594–10604 (2002).