



Ag nanoparticles as multifunctional SERS substrate for the adsorption, degradation and detection of dye molecules

Yongmei Ma^{a,1}, Qianqian Ding^{a,1}, Liangbao Yang^{b,*}, Li Zhang^{c,*}, Yuhua Shen^{a,*,1}

^a School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, PR China

^b Institute of Intelligent Machines, Chinese Academy of Science, Hefei 230031, Anhui, PR China

^c Department of Chemistry & Biology, Anhui Key Laboratory of Spin Electron and Nanomaterials (Cultivating Base), Suzhou College, Suzhou 234000, PR China

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ABSTRACT

Ag NPs were obtained by isopropyl alcohol restore silver nitrate with silicotungstic acid as a stabilizer under the condition of UV irradiation. From changing the amount of isopropyl alcohol and silver nitrate, we obtained Ag NPs of which plasmon peak was similar to the excitation wavelength, and the enhancement effect will be greatly improved. Enriching, degrading, and detecting dye molecular can be achieved by the simple SERS substrate, and the photo-degradation process was monitored by SERS successfully for the first time, and the sensitivity was improved compare to traditional detection by UV–vis spectroscopy.

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1. Introduction

Raman spectroscopy has attracted a lot of attention since the first observation of surface enhanced Raman scattering (SERS) in 1974 [1,2]. Recently, SERS has drawn much attention for its potential applications in various fields, including analytical chemistry, medical science, life science, and the characterization of trace chemical species [3–6]. However, the advantage of SERS using for monitoring photocatalytic dynamics process has not developed, most of us will use UV–vis spectrophotometer to monitor the whole process [7,8]. Because the limitations of the UV–vis spectrophotometer sensitivity, it cannot monitor the relatively low concentration of substances in the photocatalytic degradation process, thus to find a more sensitive method of monitoring is so important. In this paper, we will first use SERS to monitor photodegradation dynamics process of the organic dye molecular, it will compensate the defect of low monitoring sensitivity about UV–vis spectrophotometer and put forward the new application of SERS.

Consider the application of SERS, it is necessary to develop an efficient SERS substrate that not only can provide strong enhancement factors, but also can be reproducible and stable [9,10]. Various

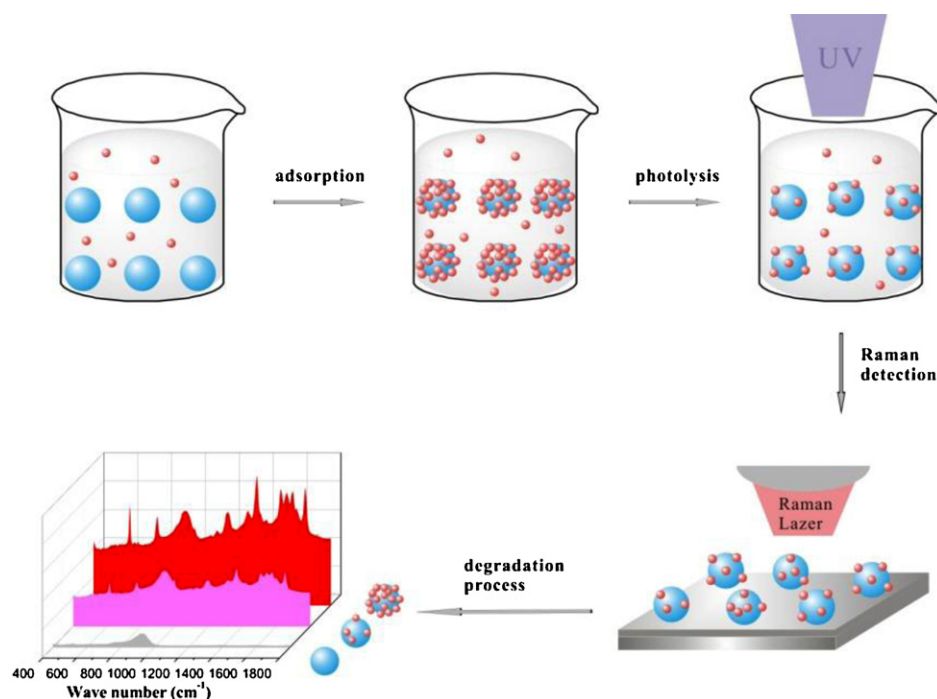
methods have been used to prepare the efficient SERS surfaces, including vapor deposition, chemical reactions, and ion-beam-sputtered technique [11–15]. Furthermore, the SERS substrate becomes cheaper and easier to be fabricated and handled are also very important for SERS as a generally analytical tool [9,16]. Consequently, reducing the cost of preparing SERS-active substrates is a natural next significant topic. The problem that traditional SERS substrates are single-use has resulted in its availability not being fully explored or recognized by the analytical scientists as a routine analytical technique. So, fabricating a multifunctional SERS substrate is an efficient and feasible method to reduce the cost of preparing SERS-active substrates. There are have some reports about the multifunctional SERS substrate, for example, Caceres and co-workers fabricate a SERS substrate comprising magnetic and silver particles encapsulated within a poly (N-isopropylacrylamide) thermoresponsive microgel for pentachlorophenol detection [17]. A multifunctional Au-coated TiO₂ nanotube as a reproducible, stable and recyclable SERS substrate for organic pollutants detection had been reported by Li and co-workers [9]. However, the multifunction of these SERS substrates is not so obvious, and most of them are too complex, the cost is also too high. So we should have further research to fabricate simple, cheap and truly multifunctional SERS substrates.

Here, we report a simple approach to prepare a multifunctional, reproducible, and stable SERS substrate, pure Ag nanoparticles, which is fabricated under the protection of tungstosilicate acid [H₄SiW₁₂O₄₀, TSA] [18]. The TSA can be used as oxidants, reducing agents, catalysts, anti-blocking agent and template agent [19–22].

* Corresponding authors.

E-mail addresses: lbyang@iim.ac.cn (L. Yang), zhliusuzh@163.com (L. Zhang), s.yuhua@163.com (Y. Shen).

¹ Fax: +86 551 5592420.



Scheme 1. Schematic illustration of multifunctional application of simple SERS substrate.

Silver is well known to improve photocatalytic properties by the reduction of electro/hole recombination reaction [23,24]. So the synthesis solution can be used for photocatalytic degradation of organic dye molecules as well as the Ag nanoparticles can be used as SERS substrates, the basal synthesis process is very simple and the cost is very low, so it achieves the purpose of obtaining the simple multifunctional SERS substrates with low-cost. And the whole dynamic process of photocatalytic degradation with Ag nanoparticles will be used in conjunction with UV–vis spectrophotometer and SERS for simultaneous monitoring the efficiency of photocatalytic degradation of organic dye molecules.

2. Experimental

2.1. Reagents

3-Aminopropyl-trimethoxysilane (APTMS), TSA, AgNO₃, isopropyl alcohol, R6G, H₂SO₄, HCl were A.R. grade and obtained from Shanghai Reagent Co. without further purification, and their solutions were prepared with ultra-pure water.

2.2. Synthesis of Ag NPs

Ag NPs were prepared by isopropyl reduction of AgNO₃. 1 ml 0.003 M AgNO₃ was added into 50 ml 5 × 10⁻⁴ M TSA, then added 49 ml ultra-pure water into the solution. 30 min later, added 4 ml isopropyl into the solution, then put the solution under the UV lamp 2 h with stirring. Then the Ag NPs in solution were collected by centrifugation and washed with ultra-pure water for two times and these Ag NPs were used as SERS substrate. The remained solution was used for photocatalytic experiment.

2.3. Experiment of absorption ability

The solution was centrifuged to collect Ag NPs, the collected Ag NPs were added into 10⁻⁵ M R6G, and Rhodamine 6G (R6G) with Ag NPs was centrifuged 2 h later. The filtrates were analyzed by

recording the variation of the absorption-band maximum in the UV–vis spectrum of R6G. And the isolated nanoparticles were analyzed by recording the variation of the absorption-band maximum in the Raman spectrum of R6G.

2.4. Experiment of photocatalytic ability

Photocatalytic activity was evaluated by the degradation of R6G under UV-light irradiation using 125 W UV lamp. In each experiment, the solution contained Ag NPs was added into R6G solution (10⁻⁵ M), and the concentration of diluted R6G solution is 2 × 10⁻⁶ M. The solution was put under UV lamp with magnetically stirred. At given time intervals, 3 ml aliquots were sampled and centrifuged to remove Ag NPs. The filtrates were analyzed by recording the variation of the absorption-band maximum in the UV–vis spectrum of R6G. And the isolated nanoparticles were analyzed by recording the variation of the absorption-band maximum in the Raman spectrum of R6G.

2.5. Modification of glasses

The glasses were pre-treated using a piranha solution (98% H₂SO₄/30% H₂O₂ = 3:1 v/v) for 30 min, followed by rinsing with ultra-pure water. Subsequently, they were treated with 1 mM 3-aminopropyl-trimethoxysilane (APTMS) of ethanol solution for 2 h at room temperature. One end of the APTMS is to glass surface while the amino end of the APTMS is used to bind the Ag NPs. The glasses were rinsed with ethanol and heated at 110 °C for 1 h. Then the glasses were added into 2% HCl for 10 min and dried under a stream of N₂ [25,26]. The Ag NPs solution was injected into sample cell, the Ag NPs are easy to adsorb to the glass from solution due to the amino of the glass surface. R6G solution was injected into sample cell after the Ag NPs solution was extracted from sample pool, the information on the surface of the glass in the sample pool was obtained by OWG [27].

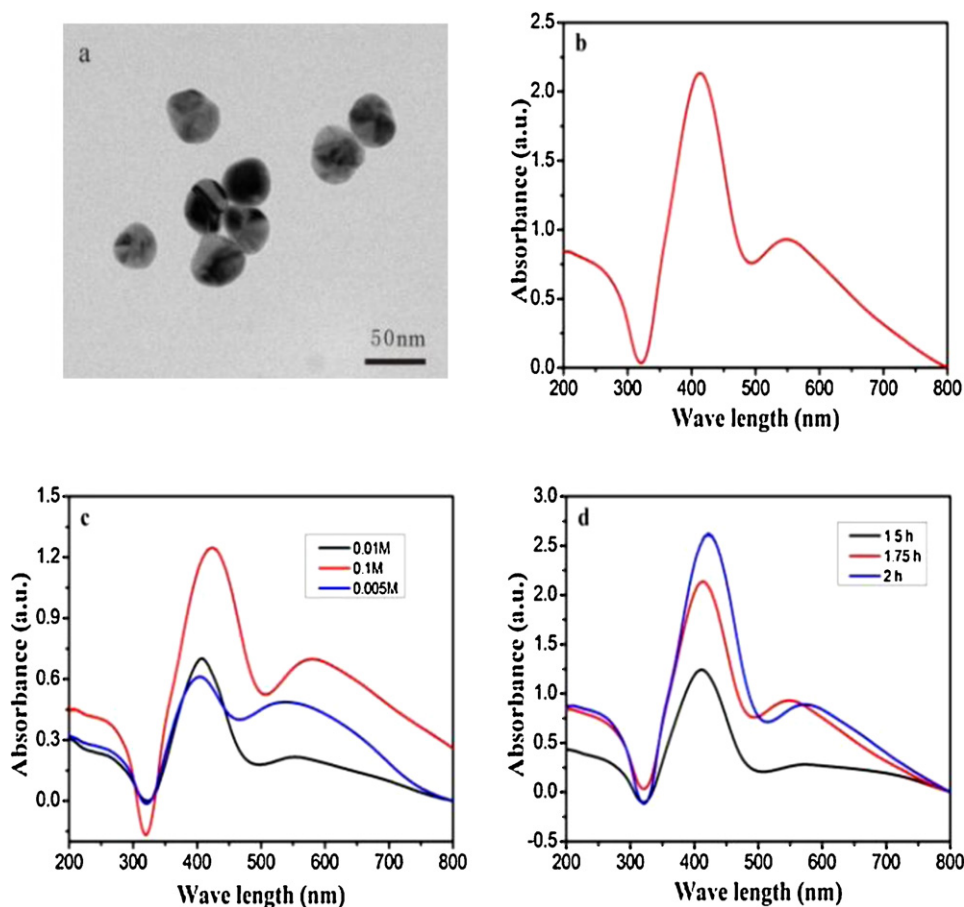


Fig. 1. (a) TEM images of Ag nanoparticles. (b) UV–vis absorption spectra of Ag nanoparticles with the best reaction condition. (c) UV–vis absorption spectra of Ag nanoparticles with different concentrate of AgNO_3 . (d) UV–vis absorption spectra of Ag nanoparticles with different illumination time.

3. Results and discussion

We fabricate a simple SERS substrate – Ag NPs based on the multifunctionality of enrichment, SERS effect and photocatalytic degradation for detection of organic dye molecular. Scheme 1 shows how the enrichment, photocatalytic degradation and SERS-active substrate works: after the enrichment of organic dye molecular on the surface of Ag NPs, the substrate can photocatalytic degradation of the organic dye molecular, and the dynamic detection of organic dye molecular based on SERS application meanwhile. The Ag NPs as multifunctional SERS-active substrates are discussed in detail through a series of experiments.

The typical TEM images of Ag nanoparticles are shown in Fig. 1a. Fig. 1a clearly shows Ag nanosphere has a uniform size distribution with a diameter about 30 nm around, and it also reveal that Ag NPs are well-dispersed without any aggregation, indicating the colloidal stability of these dispersions. Changing the amount of isopropyl alcohol and silver nitrate, we obtained Ag NPs of which plasmon peak were different with each other. The localized surface plasmon resonance (LSPR) peak associated with the silver nanoparticles at 400 nm is shown in Fig. 1b, it is worth noting that a shoulder peak appeared in the range of 540–550 nm, which could be attributed to aggregation for washing Ag NPs with ultra-pure water. Localized electromagnetic (EM) field distribution in association with surface plasmon resonance (SPR) excited at the interstitials (i.e. hot-sites) of a small aggregate in nanometric space is the prime factor for giant optical field enhancement and has attracted huge

interest in various fields of applications [28,29]. Aggregates of noble metal nanoparticles, particularly silver nanoparticles have shown their potential in various sectors of nanoscience and technology including SERS. So we changed the amount of isopropyl alcohol and silver nitrate to obtain Ag NPs of which plasmon peak were similar to the excitation wavelength, as shown in Fig. 1c and d. Fig. 1c shows the UV–vis absorption spectra of Ag nanoparticles with different concentrate of AgNO_3 and Fig. 1d shows the UV–vis absorption spectra of Ag nanoparticles with different illumination time. From the result in Fig. 1c and d, we can select the best condition to synthesize the Ag NPs easily. With the best reaction condition, we obtained Ag NPs of which plasmon peak was similar to the excitation wavelength, and the enhancement effect will be greatly improved [10,30].

Fig. 2A shows the UV–vis spectra of R6G before (a) and after (b) absorption by Ag NPs. R6G has an absorbance peak centered at 525 nm, the peak intensity of maximum absorption of pure R6G is 1.1 a.u., and the peak intensity of maximum absorption of filtrates is 0.6 a.u. after R6G solution was mixed 2 h with Ag NPs, R6G was absorption on the surface of Ag NPs for a certain time, the concentration of remaining R6G in the filtrate was decrease after centrifuged, the peak intensity of maximum absorption became weaker, the decay in the absorption peak was clearly observed compared to pure R6G. Relatively speaking, the SERS signals of R6G after absorption by Ag NPs is increase due to a mount of R6G molecular absorption on the surface of Ag NPs. Fig. 2B shows the SERS spectra of R6G before (b) and after (a) absorption by Ag NPs. The Raman

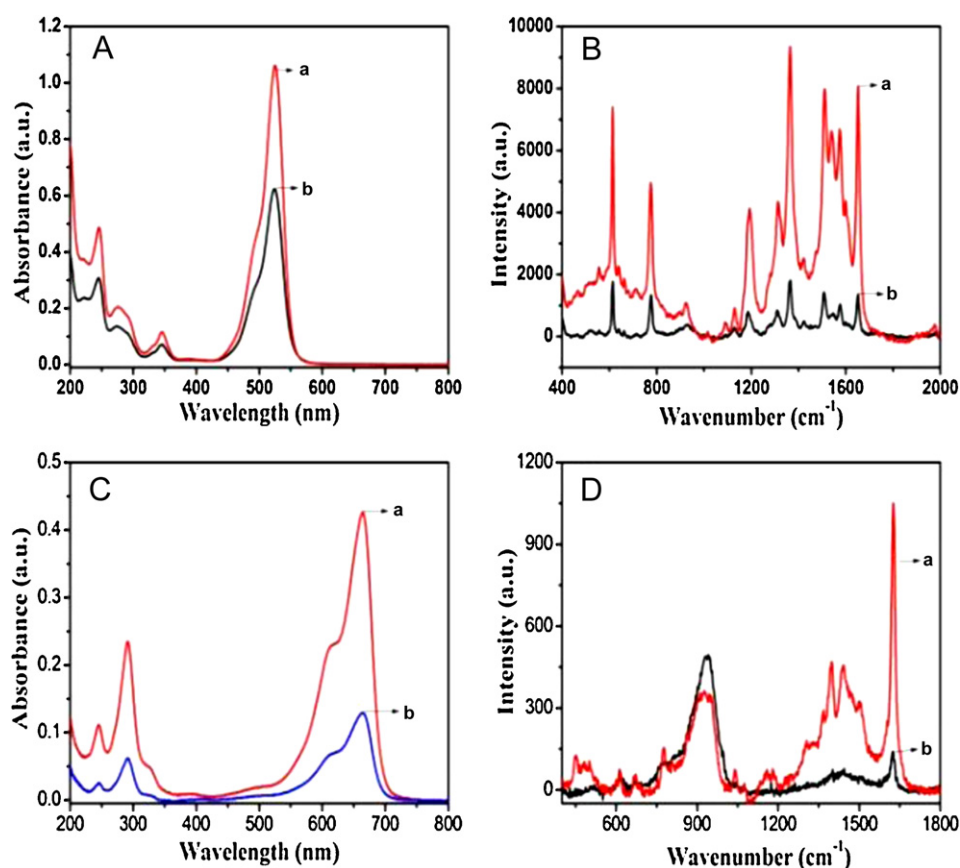


Fig. 2. (A) The UV-vis spectra of R6G before (a) and after (b) absorption by Ag NPs, (B) SERS spectra of R6G before (b) and after (a) absorption by Ag NPs, (C) the UV-vis spectra of MB before (a) and after (b) absorption by Ag NPs, and (D) SERS spectra of MB before (b) and after (a) absorption by Ag NPs.

bands at about 1650, 1576, 1508, 1364, 1186, 775, and 613 cm^{-1} can be attributed to R6G and agree well with literature data [31]. It can be found from Fig. 2B that the SERS signals of R6G increased after centrifuged to remove the filtrate. From Fig. 2A and B can clearly see that Ag NPs do have the capability to absorb the dye molecules on the surface of itself, so the UV-vis spectra of filtrate illustrate the peak intensity was weaker due to the concentration of R6G decreased. A mount of R6G molecule was absorbed on the surface of the Ag NPs, the concentration of R6G which absorption on the surface of the Ag NPs was increase, so the intensity of SERS signals became increase. Fig. 2C shows the UV-vis spectra of MB before (a) and after (b) absorption by Ag NPs. MB has an absorbance peak centered at 680 nm, the peak intensity of maximum absorption of pure MB is 0.45 a.u., and the peak intensity of maximum absorption of filtrates is 0.615 a.u. after MB solution was mixed 2 h with Ag NPs. MB was absorbed on the surface of Ag NPs for a certain time, the concentration of remaining MB in the filtrate was decrease after centrifuged, the peak intensity of maximum absorption became weaker, and the decay in the absorption peak was clearly observed compared to pure MB. Relatively speaking, the SERS signals of MB after absorption by Ag NPs is increase due to a mount of MB molecule absorption on the surface of Ag NPs. Fig. 2D shows the SERS spectra of MB before (b) and after (a) absorption by Ag NPs. And the SERS signals of MB do increased after centrifuged to remove the filtrate. From Fig. 2 can clearly see that Ag NPs do have the capability of absorbing the dye molecule on the surface of itself.

Ag NPs have the capability of absorption the dye molecular on the surface of itself can also be proved by optical waveguide (OWG)

as shown in Fig. 3. In Fig. 3, it shows the assembly process of R6G on Ag NPs modified OWG surface by pumping the R6G solution into the sample cell. As the time goes, the intensity of OWG signals became increase, from red to green, and this is only because the concentrate of R6G become higher. That is to say, Ag NPs have the capability of absorbing the dye molecule, more and more R6G molecules have been absorbed on the surface of Ag NPs.

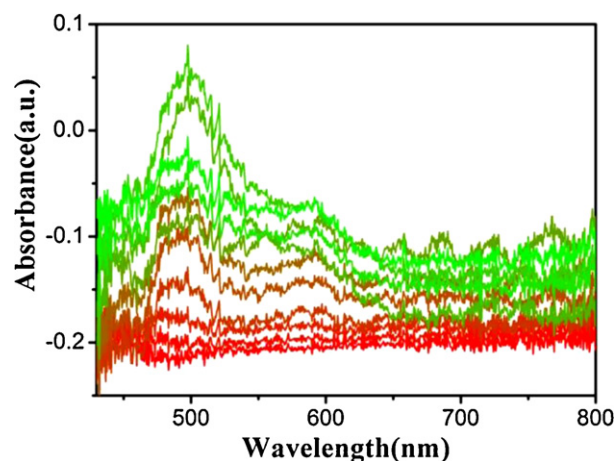


Fig. 3. The assembly process of R6G on Ag NPs modified OWG surface by pumping the R6G solution into the sample cell.

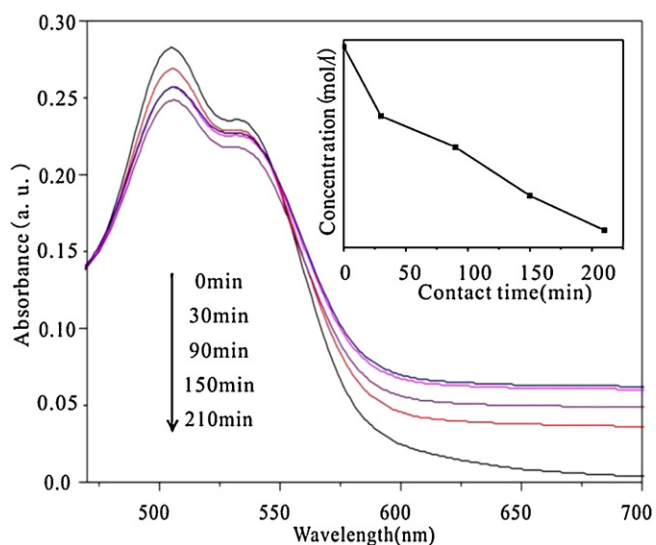


Fig. 4. The absorption spectra of R6G after photocatalytic degradation by Ag NPs after irradiation for different times. Inset: the remaining concentration of R6G after photocatalytic degradation with different irradiation times.

The Ag NPs with TSA as protection agents and photosensitizers have effect on the photocatalytic properties for photodegradation of organic dye molecule. Fig. 4 shows the absorption spectra of filtrate after centrifuged to avoid the effect of surface-plasmon resonance (SPR) from Ag NPs which were expected to be around 424 nm, has been irradiated with UV lamp at different times in the presence of Ag NPs as a photocatalyst. The maximum absorption intensity of R6G was found to decrease by increasing the irradiation time. Inset clearly shows that the remaining concentration of R6G after photocatalytic degradation with different irradiation times. With the growth in irradiation time, more and more R6G molecular has been photocatalytic degraded by Ag NPs, so the remaining concentration of R6G became decrease gradually. In order to see the dynamic process of photocatalytic degraded more clearly, we monitor the whole dynamic process by SERS spectra for the first time. Fig. 5 shows the SERS spectra of R6G of the maximum absorption at 613 cm^{-1} after photocatalytic degradation by Ag NPs after irradiation for different times. For the first 3 h, the peak intensity of absorption became increase because the absorption as dominant effect, amount of R6G molecular absorption on the surface of Ag NPs. 3 h later, the peak intensity of absorption became weaker because the photocatalytic degradation as

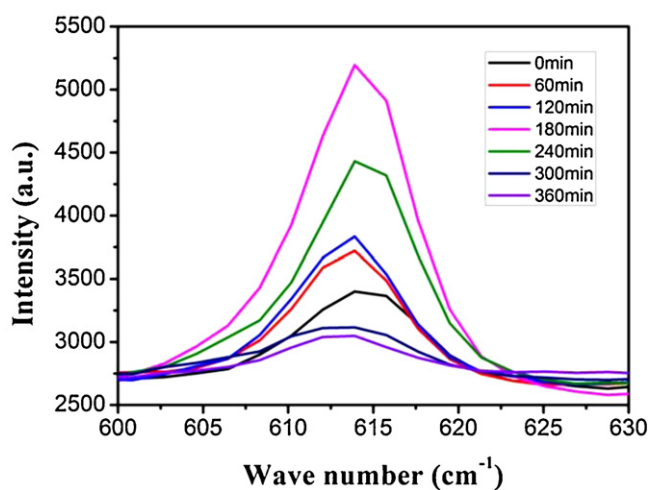


Fig. 5. The SERS spectra of R6G of the maximum absorption at 613 cm^{-1} after photocatalytic degradation by Ag NPs after irradiation for different times.

dominant effect. The dye molecular has been photocatalytic degrading gradually, the concentration of R6G on the surface of Ag NPs, so the the peak intensity of absorption became weaker. From Figs. 4 and 5 can be easily proved that Ag NPs do have the capability of photocatalytic degradation the dye molecular on the surface of itself.

Fig. 6A shows the UV–vis absorption spectra of R6G after photocatalytic degradation by Ag NPs after irradiation for different times. The absorption spectra of R6G hardly see due to the sensitivity defects of UV–vis spectra, it cannot monitor the kinetic process of photocatalytic degradation when the concentration of R6G is as low as to 10^{-6} M . Now the importance of SERS for its highly sensitivity has been appeared, the dramatic enhancement of the intensity of the SERS spectra make the characteristic peaks of R6G clear during the dynamic process of photocatalytic degradation as shown in Fig. 6B compared to the same concentration of R6G characterized by UV–vis spectra shown in Fig. 6A. At this point, we posed that the photo-degradation process was monitored by SERS successfully for the first time, and the sensitivity was improved compare to traditional detection by UV–vis spectroscopy. This may hew out a new application of the SERS technique in the future research.

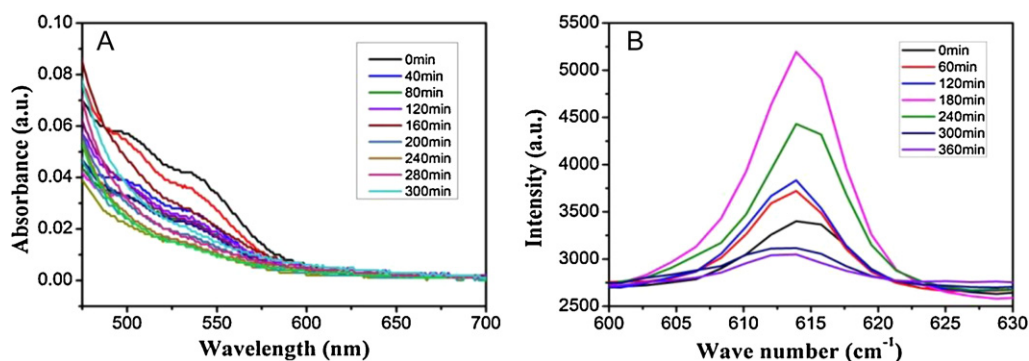


Fig. 6. The UV–vis absorption (A) and SERS (B) spectra of R6G after photocatalytic degradation by Ag NPs after irradiation for different times.

4. Conclusions

In this study, a simple method was used to synthesize the silver nanoparticles, of which the multifunction was analyzed for using as surface enhanced Raman scattering (SERS) substrate, adsorbent, and photocatalyst. We investigated the UV light-assisted photocatalytic degradation of dye molecular on Ag nanoparticles monitored by UV–vis and SERS spectroscopy. The results indicated that dye molecular was degraded effectively. Most important this study endows a new value of the SERS technique, which can be used as a new detection method for monitoring the photocatalytic processes.

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References

- [1] X.M. Lin, Y. Cui, Y.H. Xu, B. Ren, Z.Q. Tian, Surface-enhanced Raman spectroscopy: substrate-related issues, *Analytical and Bioanalytical Chemistry* 394 (2009) 1729–1745.
- [2] Y.Y. Lin, J.D. Liao, Y.H. Ju, C.W. Chang, A.L. Shiau, Focused ion beam-fabricated Au micro/nanostructures used as a surface enhanced Raman scattering-active substrate for trace detection of molecules and influenza virus, *Nanotechnology* 22 (2011) 185308–185315.
- [3] J.P. Camden, J.A. Dieringer, J. Zhao, R.P. Van Duyne, Controlled plasmonic nanostructures for surface-enhanced spectroscopy and sensing, *Accounts of Chemical Research* 41 (2008) 1653–1661.
- [4] M.D. Porter, R.J. Lipert, L.M. Siperko, G.F. Wang, R. Narayanan, SERS as a bioassay platform: fundamentals, design, and applications, *Chemical Society Reviews* 37 (2008) 1001–1011.
- [5] X.M. Qian, X. Zhou, S.M. Nie, Surface-enhanced Raman nanoparticle beacons based on bioconjugated gold nanocrystals and long range plasmonic coupling, *Journal of the American Chemical Society* 130 (2008).
- [6] W.E. Smith, Practical understanding and use of surface enhanced Raman scattering/surface enhanced resonance Raman scattering in chemical and biological analysis, *Chemical Society Reviews* 37 (2008) 955–964.
- [7] T.J. Whang, M.T. Hsieh, H.H. Chen, Visible-light photocatalytic degradation of methylene blue with laser-induced Ag/ZnO nanoparticles, *Applied Surface Science* 258 (2012) 2796–2801.
- [8] R. Ahmad, P.K. Mondal, Adsorption and photodegradation of methylene blue by using PANi/TiO₂ nanocomposite, *Journal of Dispersion Science and Technology* 33 (2012) 380–386.
- [9] X.H. Li, G.Y. Chen, L.B. Yang, Z. Jin, J.H. Liu, Multifunctional Au-coated TiO₂ nanotube arrays as recyclable sers substrates for multifold organic pollutants detection, *Advanced Functional Materials* 20 (2010) 2815–2824.
- [10] W.Y. Li, P.H.C. Camargo, X.M. Lu, Y.N. Xia, Dimers of silver nanospheres: facile synthesis and their use as hot spots for surface-enhanced Raman scattering, *Nano Letters* 9 (2009) 485–490.
- [11] C. Schmuck, P. Wich, B. Kstner, W. Kiefer, S. Schlcker, Direct and label-free detection of solid-phase-bound compounds by using surface-enhanced Raman scattering microspectroscopy, *Angewandte Chemie International Edition* 46 (2007) 4786–4789.
- [12] M.W. Shao, M.L. Zhang, N.B. Wong, D.D. Ma, H. Wang, W.W. Chen, S.T. Lee, Ag-modified silicon nanowires substrate for ultrasensitive surface-enhanced Raman spectroscopy, *Applied Physics Letters* 93 (2008) 233118.
- [13] S. Chattopadhyay, H.C. Lo, C.H. Hsu, L.C. Chen, K.H. Chen, Surface-enhanced Raman spectroscopy using self-assembled silver nanoparticles on silicon nanotips, *Chemistry of Materials* 17 (2005) 3.
- [14] V.V.R. Sai, D. Gangadean, I. Niraula, J.M.F. Jabal, G. Corti, D.N. McIlroy, D.E. Aston, J.R. Branen, P.J. Hrdlicka, Silica nanosprings coated with noble metal nanoparticles: highly active SERS substrates, *Journal of Physical Chemistry C* 115 (2011) 453–459.
- [15] X.D. Lin, V. Uzayisenga, J.F. Li, P.P. Fang, D.Y. Wu, B. Ren, Z.Q. Tian, Synthesis of ultrathin and compact Au@MnO₂ nanoparticles for shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), *Journal of Raman Spectroscopy* 43 (2012) 40–45.
- [16] V. Canpean, S. Astilean, Multifunctional plasmonic sensors on low-cost sub-wavelength metallic nanostructures arrays, *Lab on a Chip* 9 (2009) 3574–3579.
- [17] R.C. Caceres, S.A. Cela, P.G. Giros, A.F. Barbero, J.P. Juste, R.A.A. Puebla, L. Marzan, Multifunctional microgel magnetic/optical traps for SERS ultradetection, *Langmuir* 27 (2011) 4520–4525.
- [18] A. Troupis, A. Hiskia, E. Papaconstantinou, Synthesis of metal nanoparticles by using polyoxometalates as photocatalysts and stabilizers, *Angewandte Chemie International Edition* (2002).
- [19] S. Mandal, P.R. Selvakannan, R. Pasricha, M. Sastry, Keggin ions as UV-switchable reducing agents in the synthesis of Au core-Ag shell nanoparticles, *Journal of the American Chemical Society* 125 (2003) 8440–8441.
- [20] A. Sanyal, S. Mandal, M. Sastry, Synthesis and assembly of gold nanoparticles in quasi-linear lysine-keggion colloidal particles, *Advanced Functional Materials* 15 (2005) 273–280.
- [21] V. Kogan, Z. Aizenshtat, R. Neumann, Polyoxometalates as reduction catalysts: deoxygenation and hydrogenation of carbonyl compounds, *Angewandte Chemie International Edition* 38 (1999) 3331–3334.
- [22] D. Rautaray, S.R. Sainkar, M. Sastry, Ca²⁺-Keggin anion colloidal particles as templates for the growth of star-shaped calcite crystal assemblies, *Langmuir* 19 (2003) 10095–10099.
- [23] H. Limage, F.D. Tichelaar, R. Closset, S. Delvaux, R. Cloots, S. Lucas, Study of the effect of a silver nanoparticle seeding layer on the crystallisation temperature, photoinduced hydrophilic and catalytic properties of TiO₂ thin films deposited on glass by magnetron sputtering, *Surface and Coatings Technology* 205 (2011) 3774–3778.
- [24] A.S. Polo, M.K. Itokazu, N.Y.M. Iha, Metal complex sensitizers in dye-sensitized solar cells, *Coordination Chemistry Reviews* 248 (2004) 1343–1361.
- [25] C.J. Wang, J.R. Huang, J. Wang, C.P. Gu, J.H. Wang, B.C. Zhang, J.H. Liu, Fabrication of the nanogapped gold nanoparticles film for direct electrical detection of DNA and EcoRI endonuclease, *Colloids and Surfaces B* 69 (2009) 99–104.
- [26] Y. Wang, L.P. Zhu, Y.F. Zhang, M.L. Yang, Silicon nanotips formed by self-assembled Au nanoparticle mask, *Journal of Nanoparticle Research* 12 (2010) 1821–1828.
- [27] G.C.H. Rodrigo, S. Wiederkehr, M.M. Aslan, C.L. Byard, S.B. Mendes, Investigations on the Q and CT bands of cytochrome c submonolayer adsorbed on an alumina surface using broadband spectroscopy with single-mode integrated optical waveguides, *Journal of Physical Chemistry C* 113 (2009) 8306–8312.
- [28] M.K. Hossain, Y. Kitahama, G.G. Huang, X.X. Han, Y. Ozaki, Surface-enhanced Raman scattering: realization of localized surface plasmon resonance using unique substrates and methods, *Analytical and Bioanalytical Chemistry* 394 (2009) 1747–1760.
- [29] M.K. Hossain, G.G. Huang, T. Kaneko, Y. Ozaki, Surface-enhanced Raman scattering and plasmon excitations from isolated and elongated gold nanoaggregates, *Chemical Physics Letters* 477 (2009) 130–134.
- [30] A. Naravanaswamy, H.F. Xu, N. Pradhan, X.G. Peng, Crystalline nanoflowers with different chemical compositions and physical properties grown by limited ligand protection, *Angewandte Chemie International Edition* 45 (2006) 5361–5364.
- [31] X.M. Zhao, B.H. Zhang, K.L. Ai, G. Zhang, L.Y. Cao, X.J. Liu, H.M. Sun, H.S. Wang, L.H. Lu, Monitoring catalytic degradation of dye molecules on silver-coated ZnO nanowire arrays by surface-enhanced Raman spectroscopy, *Journal of Materials Chemistry* 19 (2009) 5547–5553.