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Preparation of stable core–shell dye adsorbent Ag-coated silica nanospheres as a highly active surfaced-enhanced Raman scattering substrate for detection of Rhodamine 6G

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ABSTRACT

Silica spheres are used as a template to prepare Ag-coated silica nanospheres through electrostatic interaction, using a technique of homogeneous shaking instead of magnetic stirring. Pre-synthesized spherical Ag nanoparticles are firstly adsorbed onto silica spheres through bifunctional linking molecule, the silane reagent 3-aminopropyltrimethoxysilane, to form thin silver shells. These monodispersed Ag-coated silica nanospheres are assembled onto the glass substrates, which have been functionalized by 3-aminopropyltrimethoxysilane, to form close-packed three-dimensional Ag-coated silica nanosphere arrays by electrostatic interaction. The Ag-coated silica nanospheres were investigated as substrates for surface-enhanced Raman scattering using Rhodamine 6G as a probe molecule, and the enhancement factor of the Raman signal obtained on the Ag-coated silica nanospheres is about 1.74 × 109 for R6G. Compared with pure silver hydrosols, the prepared Ag-coated silica nanospheres have a higher Raman enhancing effect. The hybrid nanosphere substrates can be used as a highly sensitive chemical and biological sensor for Rhodamine 6G dye.

1. Introduction

The conventional Raman spectra often suffer from weak signal strength, however, the discovery of surface-enhanced Raman scattering (SERS) gave birth to a convenient and sensitive technique for detecting surface adsorbates [1–3]. Noble metal nanoparticles, such as Au and Ag, exhibit locally enhanced electric fields when illuminated at their localized surface plasma wavelengths. The SERS effect is observed when probe molecules are adsorbed on noble metal surfaces. However, only probe molecules in close proximity to these surfaces, which surface plasma resonances are coupled together, could produce large electric-field enhancement in the gap between neighboring nanoparticles, that is so-called “hot spots” [4,5]. In SERS, the localized Raman signals can be enhanced a million-fold or more when the molecules were adsorbed on aggregates of colloidal metal particles or roughened metal surfaces [6,7]. In virtue of a higher sensitivity than the usual analytical techniques, many efforts have been made to prepare new SERS-active substrates, including colloidal dispersions of metal particles [8,9], metal island films [10–12], electrochemically roughened metal electrodes [13]. Among the useful substrates, silver is the most commonly used.

For solid metal substrates, the stability of the metal surfaces often influences the efficiency of the SERS substrates, but it can be significantly improved by the addition of a silica support for the noble metal [14]. The support of silica can be not only applied to disperse noble metal but also to stabilize the metallic phase. Therefore, silver nanoparticles can be uniformly distributed on the silica-supported substrate, where silica can also preserve the aggregation state of silver nanoparticles, making it possible to stabilize the SERS effect. So far, there have been core–shell structured nanoparticles to be prepared and applied as SERS-active substrates [1,5,10,15,16]. Bao and co-workers [17] prepared a new SERS substrate based on vapor deposition of silver nanoparticles on silica spheres. But although this type of substrates exhibited good stability and sensitivity, it is too complex to be fabricated conveniently, so that the substrate is not practical for SERS detection. While a large number of efforts have been focused on the study of SERS properties of different noble metal or their compounds, there have been only a few reports on the fabrication of silica-supported metal substrates.

In recent years, SERS, as a kind of highly sensitive determination technology of dyes, has attracted wide interests [18,19]. In the

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present work, a fabrication and application on recognition of Rhodamine 6G dye (R6G) of Ag-coated silica nanosphere, as highly SERS-active substrates was described. The results show that the surface morphology of the substrate was extremely favorable to the enhancement of Raman signals and it can be used for highly sensitive determination of R6G.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, 98%), 3-aminopropyltrimethoxysilane ($NH_2(CH_2)_3Si(CH_3O)_3$, APTMS, 99%), Rhodamine 6G (R6G, 98%) were purchased from Aldrich Chemical Company. Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), ammonium hydroxide (NH_4OH, 25–28%) were obtained from Shanghai Chemical Reagents Company (Shanghai, China). All other reagents were used without further purification. Glass plates were prepared by cutting fresh microscope slides into 1×1 cm pieces and were cleaned using freshly prepared 98% H_2SO_4/30% H_2O_2 (v:v) at 90 °C for at least 1 h and then rinsed with distilled water followed by ethanol and dried under a stream of clean nitrogen. All of the glassware was washed with freshly prepared aqua regia (volume ratio $HCl:HNO_3 = 3:1$).

2.1.1. Caution

H_2SO_4/H_2O_2 solution and aqua regia are very toxic chemicals and should be handled carefully!

2.2. Characterization

UV–Vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Morphological images of Ag nanoparticles were obtained with a Japan Seiko SPI-3800N atomic force microscope (AFM) in a tapping mode with a commercial Si_3N_4 probe. The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI-5702 multifunctional XPS spectrometer, using Al Kα radiation (1486.6 eV) as the exciting source, and all peak positions were normalized to the binding energy of C 1s (284.6 eV). Scanning electronic microscopy (SEM) was used to visualize the surface morphologies of silica nanospheres and Raman-active substrate on a JSM-5600LV/KVEX scanning electron microscope. Surface-enhanced Raman measurements were performed using a FT-Raman spectrometer (RFS 100/s, Bruker) with 200 mw of 1064 nm radiation from an $NdVO_4$ laser. The scan times were 50 times.

2.3. Preparation of the substrate

Uniform 200–250 nm silica spheres were synthesized by base-catalyzed hydrolysis of TEOS with the Stöber method [20]. Briefly, a mixture of ethanol (100 mL), ammonia water (5 mL), distilled water (3 mL) and TEOS (2 mL) was stirred overnight at room temperature. The resulting silica spheres were then washed and centrifuged three times in ethanol. Subsequently, the surface of the silica spheres was functionalized with amino groups by APTMS treatment in ethanol. Spherical Ag nanoparticles were prepared by reducing $AgNO_3$ with $NaBH_4$ in the presence of citrate as a stabilizer. In a typical preparation, a sodium citrate solution (0.2 mL, 1%) was first added to $AgNO_3$ solution (20 mL, 0.01%) under homogeneous shaking for 1 min, and then, a freshly prepared ice-cold $NaBH_4$ solution (1 mL, 0.075%) was injected all at once under vigorous shaking, the solution immediately turned yellow, indicating the formation of Ag nanoparticles. These nanoparticles were used within 24 h of their preparation. To assemble these Ag nanoparticles onto silica spheres, APTMS-functionalized silica spheres (20 mg) were dispersed into the Ag nanoparticle solution (10 mL) by sonication, and then shaking for 12 h, this Ag-coated silica nanospheres were collected by centrifugation and then redispersed into a citrate solution (10 mL, 1%) for 30 min in order to enhance further adsorption of the Ag nanoparticles onto the silica spheres. Then, the Ag-coated silica nanospheres (5 mg) were dispersed into water (10 mL), APTMS-functionalized glass plates were immersed in the solution for 6 h to assemble Ag-coated silica nanospheres on them, forming close-packed three-dimensional Ag-coated silica nanosphere arrays by electrostatic interaction. Typically, clean glass plates were functionalized with APTMS by immersing them in an acetone solution of APTMS (10 mmol) for 30 min, rinsing them with acetone, and then drying at room temperature. Finally, different concentrations of R6G were adsorbed onto such obtained SERS-active substrates for detecting their Raman signals. The preparation procedure of SERS-active Ag-coated silica nanoshperes was illustrated in Fig. 1.

2.4. Adsorption of R6G on Ag-coated silica substrates

R6G sample solutions were prepared in the concentration range of 1×10^{-4} mol L^{-1} to 1×10^{-7} mol L^{-1} for SERS measurements. And then respectively immerse SERS-active substrates in R6G solutions with different concentrations for 3 h to adsorb R6G molecules on the surface of the substrate. The SERS substrate plates were removed from the R6G solution and the solvent was allowed to evaporate.

3. Results and discussion

3.1. Characterization of SERS-active Ag-coated silica substrates

To synthesize SERS substrates, silica spheres with a diameter of 200–250 nm were prepared using the well-known Stöber method, as shown in Fig. 2. These silica spheres were then functionalized with APTMS to introduce amino groups onto their surfaces to acquire positively charged surfaces.

Fig. 3 shows thermogravimetry of APTMS modified SiO_2 nanopheres. There are two obvious weight loss peaks. Loss of adsorbed water occurs before 100 °C and oxidation and decomposition of grafted APTMS starts 250 °C with an approximate 10% of weigh loss. These results indicate that about 10% APTMS of SiO_2 mass has been grafted on the surface of silica nanopheres.

Silver nanoparticles with an average size of ~15 nm obtained by reduction by $NaBH_4$ are adsorbed onto the APTMS-functionalized silica surface by electrostatic interaction to form a thin silver shell. It is known that alkylamines exist predominantly as positively charged $R{-}NH_3^+$ groups at values of $pH < 10$ [21], and reduction of Ag^+ with excess $NaBH_4$ was helpful to forming small silver nanoparticles with a net negative interfacial charge [22]. Fig. 4 shows the AFM image of the obtained silver nanoparticles, it can be seen that the silver nanoparticles are uniform and the approximately diameter is 15 nm.

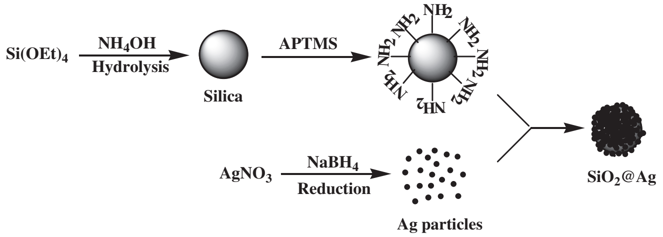

Fig. 1. Preparation procedure of a silver nanoshell on the silica sphere.

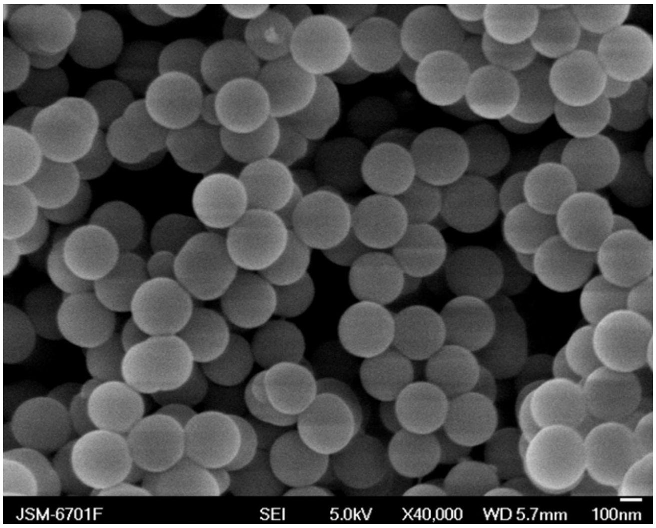

Fig. 2. SEM image of silica spheres with the diameter of 200–250 nm.

Fig. 5 shows UV–Vis spectra of silver nanoparticles and silver-coated silica. When the silver nanoparticles coat the silica spheres as a thin shell, there is an increase in the intensity of the plasma absorption and a red shift in the maximum absorption peak from 389 to 402 nm. It is due to the fact that the local refractive index around the silver particles increases after attaching silica spheres.

Fig. 6 shows the XPS spectra of Ag-coated silica nanospheres, it is obviously found that the two typical Ag3d characteristic peaks, respectively located at 367.7 eV and 373.4 eV, strongly support the presence of silver.

Fig. 7 is the SEM image of a typical SERS-active substrate formed by Ag-coated silica nanospheres. The close-packed three-dimensional Ag-coated silica nanosphere arrays were assembled on an APTMS-functionalized glass plate through electrostatic interaction. An enlarged SEM image was inserted on Fig. 7 in order to distinguish the morphology of silver. It was clear that there was a mass of nanometer-sized silver particles covering the surface of silica sphere, forming thin silver shells. Therefore, these silver shells are primarily responsible for the enhancement of Raman signals.

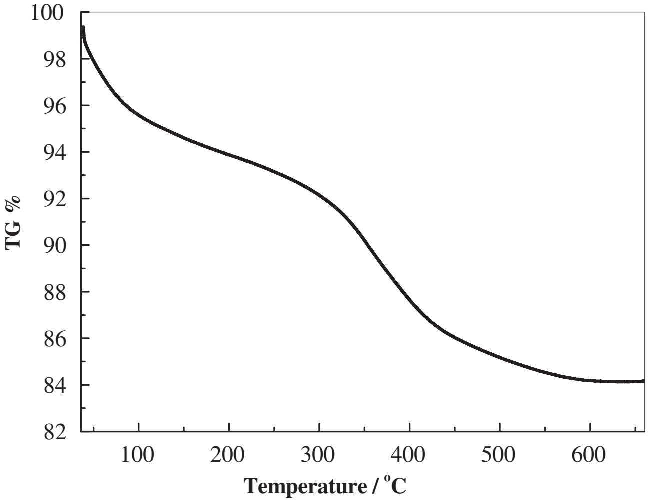

Fig. 3. Thermogravimetry of APTMS modified SiO_2 nanopheres.

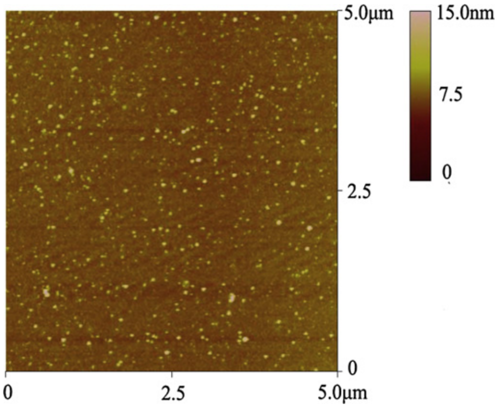

Fig. 4. AFM image of silver nanoparticles.

3.2. SERS measurements of R6G

SERS has been applied as a convenient and sensitive technique to investigate surface adsorbates. The Raman scattering signal can be amplified when SERS-active molecules are spatially confined within the range of locally enhanced electric fields. Here R6G was used here as reference to verify the spectral efficiency of the new substrates. Fig. 8 shows the SERS spectra of R6G with different concentrations adsorbed on Ag-coated silica nanosphere substrates. Because 1064 nm of laser initiated the strongest Raman signal for R6G, it was chosen as an excitation wavelength in further experiments. The observed Raman bands at 1650, 1597, 1510, 1361, 1313 and 1184 cm^{-1} can be respectively attributed to υ(C–C) stretching vibrations of R6G molecules and agree well with values in the literature [23]. In order to estimate the enhancement factor, SERS spectra were also recorded on dry R6G powders (Fig. 8, curve e). The intensity of the υ(C–C) stretching vibration mode of R6G at 1510 cm^{-1} was used to calculate the enhancement factor.

The enhancement factor (EF) was calculated according to the formula [24],

$$\text{EF} = \left(I_{\text{SERS}} \times N_{\text{powder}}\right) \Big/ \left(I_{\text{powder}} \times N_{\text{SERS}}\right)$$

where, $I_{\text{SERS}} = 0.02021 = 2.201 \times 10^8$ cps, denote the surface-enhanced Raman intensity, $I_{\text{powder}} = 0.00077 = 7.7 \times 10^6$ cps, is the Raman intensity of the powder sample, N_{SERS} is number of the radiated R6G molecules adsorbed on the Ag-coated silica

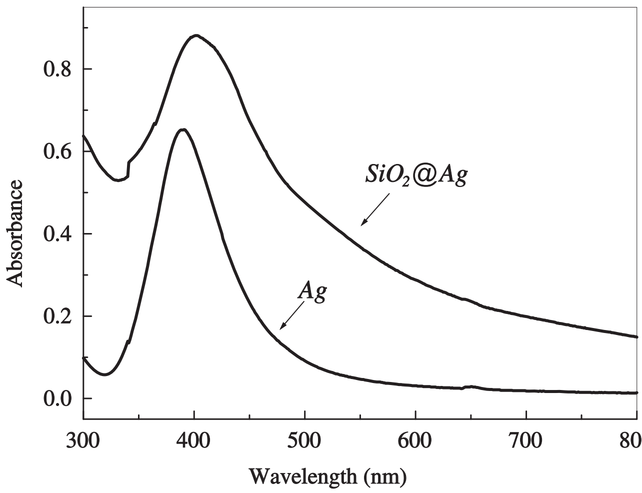

Fig. 5. UV–Vis spectra of silver nanoparticles and Ag-coated silica nanospheres.

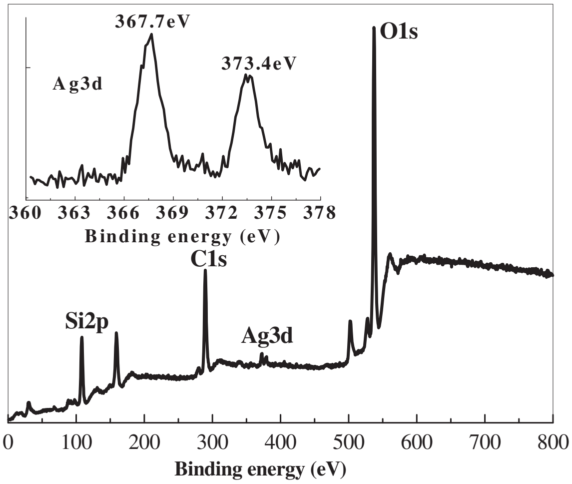

Fig. 6. XPS spectra of the Ag-coated nanospheres at wide-scan and Ag 3d (inset).

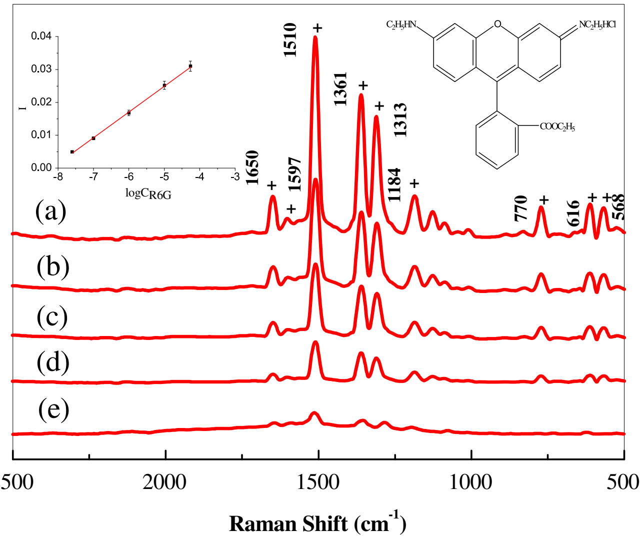

Fig. 8. SERS spectra of R6G of different concentrations adsorbed on the Ag-coated silica nanosphere substrate. [R6G]/(mol L^{-1}): a) 1×10^{-4}; b) 1×10^{-5}; c) 1×10^{-6}; d) 1×10^{-7}; e) Dry R6G powders. In addition, these spectra have been shifted vertically for clarity.

nanospheres assembled on the glass plate, equal to RA/σ, where $R = 1.05$, is the surface roughness factor, A is an area of the laser focus and σ is adsorption area of a R6G molecule on the film, and N_{powder} is number of the radiated R6G molecules in the powder sample, equal to $AhcN_A$, where $h = 5.2 \times 10^{-5}$ m, is effective focusing depth of laser, $c = 1.0 \times 10^{-4}$ mol L^{-1}, is the concentration of R6G in the solution, and N_A is Avogadro's constant, 6.02×10^{23} mol^{-1}.

According to the calculation result of the semiempirical molecular orbital method of Gupta et al. [25], σ equals to 222 Å.

After the background was deducted, the enhancement factor of the Raman signals for the Ag-coated silica nanospheres was calculated as 1.74×10^9.

Further study showed that when the concentration of R6G was from 2.5×10^{-8} mol L^{-1} to 5.0×10^{-5} mol L^{-1}, the peak height at 1510 cm^{-1} was directly proportional to logarithm of the concentration, and the regression equation was $I = 0.06434 + 0.00786\lg C_{R6G}$ with a relative coefficient of 0.9996 and a standard deviation of 3.6×10^{-5}($n = 5$). The detection limit was down to 9.0×10^{-9} mol L^{-1}.

Silver hydrosol was commonly used as SERS substrate [26], silver nanoparticles were deposited on silicon or glass slides. Compared with sliver hydrosol substrate, Ag-coated silica nanosphere substrate exhibited a higher SERS activity. Fig. 8 shows the comparison of SERS spectra between the two types of substrates, which adsorb the same concentration of R6G (1×10^{-6} mol L^{-1}). It is obvious that the intensity of Raman signals obtained on Ag-coated silica nanosphere substrate (Fig. 9, curve a) is greater than that from sliver hydrosol substrate (Fig. 9, curve b). It is known that the signal enhancement of silver nanoparticles deposited on glass plates was primarily due to the electric-field enhancement associated with individual silver nanoparticles and the presence of a small number of aggregated silver nanoparticles. Silver nanoparticles assembled on silica contain three types of nanoparticle arrangements, such as isolated nanoparticles, surface-plasma coupled nanoparticles, and aggregated nanoparticles. The electric-field enhancement associated with surface-plasma-coupled nanoparticles is much larger than the enhancement associated with isolated nanoparticles, that is because the enhancement increases rapidly when the spacing between neighboring nanoparticles reduces, so the Raman signal enhancement

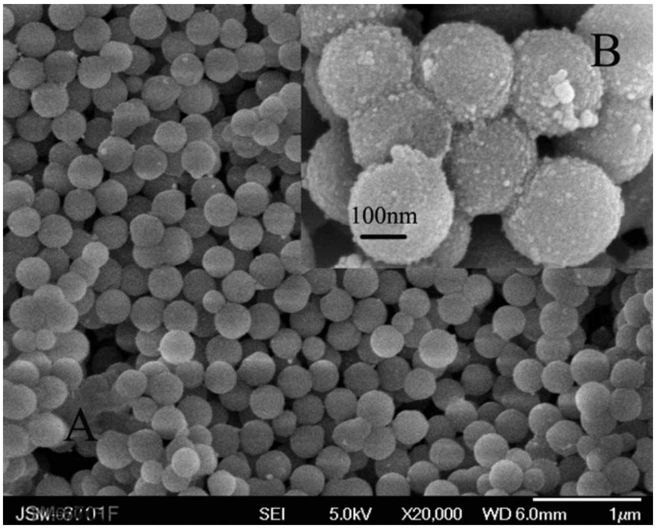

Fig. 7. SEM images of SERS-active Ag-coated silica substrate.

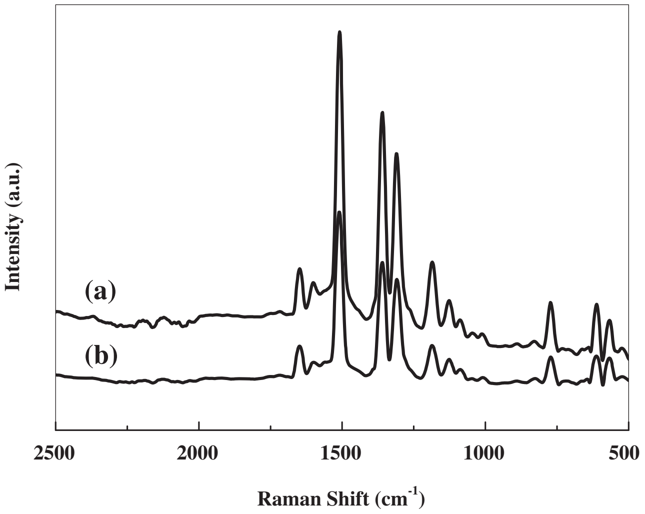

Fig. 9. SERS spectra of R6G adsorbed on a) Ag-coated silica nanosphere substrate, b) silver hydrosol substrate.

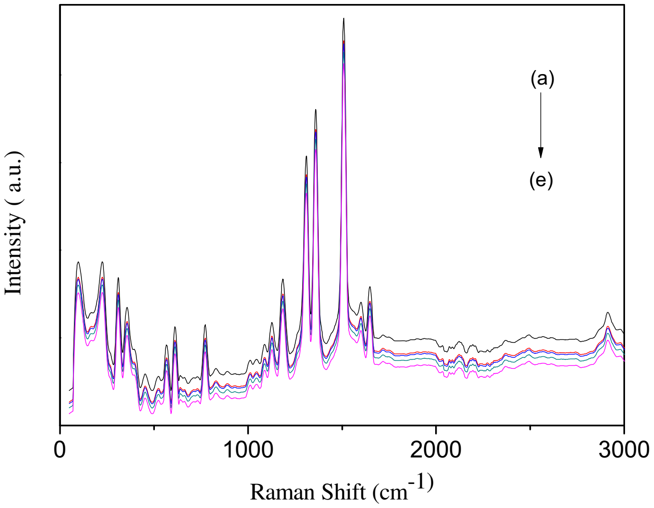

Fig. 10. SERS spectra of R6G adsorbed one Ag-coated silica nanosphere substrate, repeating the process *adsorbing-rinsing-adsorbing* for four times, b)–e); a) is the original spectra before the first rinse.

should mainly occur on both surface-plasma-coupled and aggregated nanoparticles.

In order to evaluate the stability and efficiency of Ag-coated silica nanosphere substrates, the substrate adsorbing 1×10^{-6} mol L^{-1} R6G is first measured, the SERS spectra are shown in Fig. 10(a). It can be seen that the Raman signals are quite strong. After the substrate is immersed into ethanol for a few minutes and adsorbed R6G molecules are rinsed and removed, the Raman signal disappears. It is interesting that when R6G is re-adsorbed on the substrate, strong signals are obtained again, as shown in Fig. 10(b–e). After above *adsorbing-rinsing-adsorbing* processes are repeated for four times, the signal intensity maintains still more than 95.5% of the original and no significant signal reduction was found. The results indicate that prepared SERS-active substrates are stable and reusable.

4. Conclusions

In summary, Ag-coated silica nanospheres are fabricated through a method of electrostatic interaction, the hybrid nanospheres can be used as an effective SERS substrate. The size of SiO_2 spheres and Ag nanoparticles are 200–250 nm and 15 nm respectively. R6G adsorbed on the substrate exhibits strong Raman signals, resulting from surface plasma coupling between closely spaced Ag nanoparticles and aggregated Ag nanoparticles, and the Raman enhancement factor of R6G was 1.74×10^9. On a given concentration range of R6G, the Raman peak height is directly proportional to the logarithm of the concentration of R6G, which can be used to sensitively determine to this dye.

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