Invited Article

Stretchable plasmonic substrate with tunable resonances for surface-enhanced Raman spectroscopy

Jinxiu Wen, Hongbo Zhang, Huanjun Chen, Weihong Zhang and Jian Chen

1 Instrumental Analysis and Research Center, Sun Yat-sen University, Guangzhou, 510275, People’s Republic of China
2 State Key Laboratory of Optoelectronic Materials and Technologies, Guangdong Key Laboratory of Display Material and Technology, Sun Yat-sen University, Guangzhou 510275, People’s Republic of China
3 School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, People’s Republic of China

E-mail: chenhj8@mail.sysu.edu.cn and pusej@mail.sysu.edu.cn

Received 23 April 2015, revised 2 July 2015
Accepted for publication 29 July 2015
Published 23 October 2015

Abstract
Transparent and flexible functional nanostructures are very important for flexible electronic devices, such as roll-up displays, handheld portable devices, and wearable electronics, and have attracted growing scientific and industrial interest in recent years. We produced a facile and flexible hybrid structure by conjugating plasmonic nanostructures onto the surface of a poly(dimethylsiloxane) (PDMS) elastomer. Such flexible hybrids were able to remarkably enhance Raman scattering from small molecules. Most interestingly, we showed that by taking advantage of the excellent flexibility of the PDMS, the plasmonic resonances of the hybrid structure could be easily tuned via external compression force. This allows for further enhancing the Raman scattering by tailoring the plasmon of the hybrid structure in resonance with the incidence laser. We believe that these properties can make the hybrid structure an excellent, flexible SERS substrate that will be of great importance in life science, medicine, and food security sensing applications.

Online supplementary data available from stacks.iop.org/JOPT/17/114015/mmedia

Keywords: surface-enhanced Raman spectroscopy, (Au core)-(Ag shell) nanorods, PDMS, stretchable, plasmon coupling

1. Introduction

In recent years both scientific and industrial communities have shown growing interest in transparent and flexible nanostructures, which exhibit great potential in flexible electronic devices, such as roll-up displays, handheld portable devices, and wearable electronics [1–5]. Flexible sensors capable of monitoring physiological and biomechanical signals from the human body are particularly important for life science, and can pave the way for the design of body sensor networks (BSN) for personalized healthcare [6–9]. On the other hand, surface-enhanced Raman spectroscopy (SERS),
distinguished by its noninvasive, non-labeling, fingerprint-type way of sensing, and ultrahigh sensitivity, has been considered one of the most promising sensing techniques for low-dose sensing applications [10–13]. For these reasons, flexible architectures with superior SERS activity are expected to be integrated into future BSN, which will allow for real-time tracing of small changes in the human skin.

A prerequisite for the SERS are substrates with significant and reproducible electromagnetic field enhancement. The most-studied nanostructures as SERS substrates are coinage metal nanostructures, such as Au, Ag, and Cu, due to their intriguing behavior of focusing light at nanoscale, derived from their plasmonic resonances [14–17]. The regions with enhanced electric fields were the so-called 'hot spots' that were responsible for the SERS activity of the nanostructures. To optimize the SERS performance, the plasmon wavelengths of the metal nanostructures should usually be tuned in resonance with the incidence light, whereby both the excitation and the Raman scattering processes can experience strong electric field enhancement due to the small Stokes shift [18–20]. However, the plasmonic properties of the metal nanostructures are usually fixed once they have been prepared. Therefore one needs to carefully choose metal nanostructures with the proper geometries for different applications, which remains cumbersome for the integration of SERS substrates. In this regard, a substrate of facely tunable plasmonic resonances within a single batch of metal nanostructures will greatly benefit the design and fabrication of SERS substrates.

Here we propose a facely fabricated and highly stretchable hybrid platform as an efficient SERS substrate with tunable plasmon wavelengths. The substrate was obtained by uniformly conjugating (Au core)–(Ag shell) nanorods onto the surface of the PDMS elastomer. Note that similar stretchable plasmonic substrates based on metal nanocrystal–modified PDMS have been demonstrated before [21–23]. For example, Chumanov et al have proposed a novel technique for embedding metal nanoparticles into a free-standing PDMS film, whereby efficient and reliable stretchable plasmonic substrates can be obtained [22, 23]. Although these substrates all show interesting plasmonic resonance properties as well as SERS activity, most of them employed single-element nanocrystals with spherical shapes. In addition, the tunability of the plasmonic properties of the stretchable substrates remains mostly unexplored. In our study we instead chose elongated nanostructures composed of Au nanorods coated with Ag shells. In comparison to their spherical counterparts, the nanorods usually exhibit synthetically tunable plasmon resonances in a wider wavelength range with much stronger electric field enhancements. In addition, incorporation of the Ag shell can further enhance the electric fields nearby [24, 25]. Both of these merits can greatly improve the SERS performance of the hybrid structures. In our study, the density of the (Au core)–(Ag shell) nanorods on the PDMS were controlled to give well-defined plasmon resonances. The hybrid substrates were shown to exhibit outstanding SERS activity, with a demonstrated Raman enhancement factor up to $5.7 \times 10^3$ using 4-methylbenzenethiol (4-MBT) molecules as the probe molecules. Most interestingly, by virtue of the excellent elastic properties of the PDMS, we showed that the plasmon resonances of the hybrid substrates could be reversibly tuned by applying and releasing external compression force on the PDMS. Such tunability was associated with the plasmon coupling between different nanorods due to the changes in their separations along with the compression or stretching of the PDMS. In this way, the plasmon peaks of the hybrid structure can be tailored to be in resonance with the incidence laser, further enhancing the Raman signal. In applications employing different excitation wavelengths, one can use the same piece of flexible SERS substrate by tuning its plasmon wavelength in resonance with the laser under simple compression. This is an advantage of the flexible SERS substrate in comparison with regular substrates. We strongly believe that the proposed hybrid structures can provide guidelines for the design and fabrication of flexible and tunable platforms for various surface-enhanced spectroscopies that will be widely utilized in future medical and biological sensing applications.

2. Methods

Hydrogen tetrachloroaurate (HAuCl₄·3H₂O, 99.99%), silver nitrate (AgNO₃, 99.99%), sodium borohydride (NaBH₄, 99.99%), ascorbic acid (AA, 98%), octadecyltrimethoxysilane (OTS, 99.9%), 4-MBT (99%), and hexadecyl trimethyl ammonium chloride (CTAC, 99%) were purchased from Sigma-Aldrich (USA). Cetyltrimethylammonium bromide (CTAB, 99%) was obtained from Kermel (Tianjin, China). The ethanol and hydrochloric acid used were of analytical reagent grade. Deionized water was used throughout the experiments.

The Au nanorods were synthesized using the seed-mediated method [26, 27]. Briefly, the seed solution was prepared by adding an aqueous HAuCl₄ solution (0.25 mL, 0.01 M) to a CTAB solution (9.75 mL, 0.1 M). Afterwards the solution was mixed by inversion. A freshly prepared, ice-cold aqueous NaBH₄ solution (0.6 mL, 0.1 M) was then added, followed by rapid inversion-mixing for 2 min The resulting CTAB-stabilized Au nanocrystal seed solution was kept at room temperature for 2–6 h before use. The growth solution was made by the sequential addition of HAuCl₄ (2.0 mL, 0.01 M), AgNO₃ (0.4 mL, 0.01 M), HCl (0.16 mL, 5 M), and AA (0.32 mL, 0.1 M) to the CTAB solution (40.0 mL, 0.1 M). To obtain the Au nanorods, 250 μL of the seed solution was then added to the growth solution. The whole mixture was left undisturbed at room temperature overnight.

The (Au core)–(Ag shell) nanorods were prepared according to our previously reported procedures [25]. Specifically, 2 mL of the as-prepared Au nanorod solution was centrifuged and redispersed into aqueous CTAC solutions (0.08 M) at the same volume. Subsequently, 240 μL of AgNO₃ (0.01 M) and 120 μL of AA (0.1 M) were added to induce the coating of the Ag shells. The resultant solutions were kept in an isothermal oven at 65 °C for 4.5 h. The
growth time of 4.5 h was used in all of the syntheses in order to make the reduction of AgNO₃ as complete as possible. Core–shell nanorods with various plasmon wavelengths can be obtained by changing the amount of AgNO₃ and AA.

Functionalization of the SERS substrate with the 4-MBT molecules was performed by immersing the PDMS substrate conjugated with the (Au core)–(Ag shell) nanorods in an ethanol solution of 4-MBT (10 mM, 10 mL) and incubating for 8 h. The substrate was then taken out and washed thoroughly with copious amounts of ethanol and deionized water. The functionalized substrate was dried with N₂ flow before the Raman measurements.

The extinction spectra were recorded using two methods. For measuring the extinction spectra of colloidal samples and hybrid PDMS substrates with large areas, a SHIMADZU UV/visible/near-infrared spectrophotometer with an incidence spot size of 5 mm was utilized. For measuring the extinction spectra of the regions corresponding to the SERS characterizations on the hybrid PDMS substrate, a microspectrometer (CRAIC Technology) with an incidence spot size of 1–2 μm was employed. The corresponding collection zones of the conventional spectrophotometer and microspectrophotometer are ∼20 mm² and ∼3 μm², respectively.

The morphologies of the nanorods were characterized using a Tecnai™ G2 Spirit transmission electron microscope (TEM) operating at 120 kV. HAADF-STEM and EDX measurements were conducted on the same TEM with operating voltage of 300 kV. The Raman spectra were collected using a Renishaw inVia microRaman spectroscopy system with a 633 nm laser as excitation source. The laser beam was focused onto the samples through a 50× objective (NA = 0.8), and the Raman signals were collected through the same objective in a back-scattering geometry. The laser power was kept at 0.17 mW. All of the spectra were obtained with an acquisition time of 10 s and by integrating for 3 times.

3. Results and discussion

Elongated metal nanorods usually exhibit two types of plasmon resonances, the transverse plasmon mode associated with electron oscillations along the diameter direction and the longitudinal mode due to electron oscillations along the length direction. The longitudinal plasmon modes are strongly dependent on the aspect ratios of the nanorods, the dielectric properties of the surrounding environment, and the compositions of the nanorods. In our study, the longitudinal plasmon wavelengths of the (Au core)–(Ag shell) nanorods can be controlled by tailoring the thicknesses of the Ag shells with different amounts of AgNO₃ and AA solutions using the same starting Au nanorods (figure S1(a), supporting information, available at stacks.iop.org/JOPT/17/114015/mmedia). Figure 1(a) gives the extinction spectra of two representative (Au core)–(Ag shell) nanorod samples. The starting Au nanorod sample exhibited a plasmon wavelength of 743 nm. By adding 240 μL and 300 μL of AgNO₃ (0.01 M) into the nanorod solution to induce the growth of the Ag coating, the plasmon wavelengths of the core–shell nanorod samples were shifted to 630 nm and 593 nm, respectively. The morphologies of the Au nanorods and (Au core)–(Ag shell) nanorods can be seen clearly from the TEM images (figures 1(b)–(d)). Both of the pristine Au nanorods and

Figure 1. Extinction spectra, TEM images, and elemental map of the pristine Au nanorod and the (Au core)–(Ag shell) nanorod samples. (a) Extinction spectra of the pristine Au nanorod (black) and (Au core)–(Ag shell) nanorod samples. The added AgNO₃ (0.01 M) for the core–shell nanorod samples were 240 μL (red) and 300 μL (blue), respectively. The volume of the added AA solution at 0.1 M was equal to half the volume of AgNO₃ for each sample. The numbers indicate the plasmon wavelengths. (b) TEM image of the pristine Au nanorods. (c), (d) TEM images of the (Au core)–(Ag shell) nanorod samples grown with 240 μL and 300 μL of AgNO₃, respectively. (e) Merged elemental map of Au nanorods with Ag shells. The red and green colors in the elemental map stand for Au and Ag, respectively.
core–shell nanorods exhibited uniform size and shape distributions. The successful coating of the Ag shells can be seen from the merged elemental map shown in figure 1(e), which indicates that each Au nanorod was wrapped by a Ag shell. The average length, diameter, and aspect ratio of the pristine Au nanorods are $60 \pm 5$ nm, $15 \pm 2$ nm, and $4 \pm 0.5$ nm, respectively. The thicknesses of the Ag shells were controlled by the amount of AgNO$_3$ (figures S1(b)–(e), supporting information). With more AgNO$_3$ added, the Ag shells will be enlarged. For the (Au core)–(Ag shell) nanorod samples represented by the red extinction curve shown in figure 1(a), the mean thicknesses of the Ag shells at the sides and ends of the nanorods are $12.5 \pm 1$ nm and $10.5 \pm 0.5$ nm, respectively. Such nonuniform coating was due to the anisotropic growth of the Ag shells on different crystal faces of the Au nanorods. The growth of the Ag shells along the transverse direction of (110) faces was faster than that in the longitudinal direction [28]. Therefore the Ag shells were thicker at the sides, leading to a decrease in the aspect ratios of the core–shell nanorods [28, 29].

For preparation of the stretchable SERS substrate, the (Au core)–(Ag shell) nanorods were first deposited onto a glass slide or silicon substrate with a 300 nm oxide layer (SiO$_2$/Si) and then conjugated to the surface of the PDMS elastomer using a transferred procedure [30]. Briefly, a cover glass slide or SiO$_2$/Si substrate was first immersed carefully in aqua regia for 1 h. Thereafter it was rinsed with deionized water and underwent an ultrasonic bath in deionized water for 30 min. For deposition of the nanorods, 2 mL of the (Au core)–(Ag shell) nanorod sample with plasmon wavelength of 630 nm was centrifuged twice to remove the CTAB and then redispersed into deionized water at the same volume. The CTAB concentration in the final colloidal nanorod solution was estimated to be $\sim 2 \mu$M. The glass slide or SiO$_2$/Si substrate was then immersed in the nanorod solution and incubated overnight to allow for the adsorption of the nanorods (figure 2(a)) [31]. After the (Au core)–(Ag shell) nanorods have been adsorbed onto the glass slide, O$_2$ plasma (2 min, 18 W, Harrick Scientific, PDC-32G) was utilized to treat the substrate and remove the residual CTAB from the nanorods. The glass slide or SiO$_2$/Si substrate was then immersed in a 1% toluene solution of OTS and kept at 55°C for 24 h (figure 2(b)). Afterwards, a mixture of Sylgard 184 elastomer and curing agent ($w/w = 10:1$) was poured onto the glass slide or SiO$_2$/Si and heated at 65°C for 12 h (figure 2(c)). After curing, the (Au core)–(Ag shell) nanorods were successfully conjugated onto the surface of the PDMS by simply peeling off the elastomer from the glass slide or SiO$_2$/Si (figure 2(d) and (e)). The resulting substrate was highly stretchable and readily used for Raman characterizations (figure 2(f)).

For SERS activity it is very important for the stretchable substrate to exhibit well-defined plasmonic resonances, which means that the core–shell nanorod should have a dispersive distribution onto the PDMS elastomer without aggregation. Under these circumstances, the plasmon resonances of the nanorods can be maintained. The preparation processes for the stretchable substrate described in figure 2 can fulfill this requirement. As shown in figure 3(a), the (Au core)–(Ag shell) nanorods have a uniform distribution on the SiO$_2$/Si substrate. The nanorod density is $30 \pm 3/\mu$m$^2$, with an average separation between the nanorods of $111 \pm 7$ nm (figure S2, supporting information). Plasmon coupling between adjacent nanorods can be avoided due to the relatively large separations ($>50$ nm) between adjacent nanorods. Due to the intact transferring process (figure 2(c) and (d)), the

![Figure 2. Schematic showing the preparation of the stretchable SERS substrate.](image)
nanorods retained their dispersive distributions on the PDMS (figure S3, supporting information). As a result, the hybrid stretchable substrate can exhibit well-defined plasmonic resonances similar to those of the freestanding core–shell nanorods. Figure 3(b) shows the comparison of the extinction spectra of the hybrid substrate and (Au core)–(Ag shell) nanorods deposited onto the glass slide. The plasmon spectra of these two samples showed similar profiles, with that of the hybrid substrate redshifted from 525 to 611 nm. The redshift was due to an increase of the refractive index for nanorods conjugated onto the PDMS elastomer. The PDMS substrate exhibits a refractive index of 1.40, which is slightly smaller than that of the glass ($n \approx 1.55$). When an individual nanorod was deposited onto the glass, only one facet in six was in contact with the glass surface. The other five facets faced the air. Therefore, the effective refractive index felt by the nanorod was around 1.09 ($\left(\frac{5}{6} + \frac{1.55}{6} \approx 1.09\right)$). On the other hand, when the nanorod was conjugated onto the PDMS, almost five facets of the nanorod were immersed in the PDMS, with only the left facet facing the air. The effective refractive index of the nanorod was increased to around 1.33 ($\left(\frac{5 \times 1.40}{6} + \frac{1}{6} \approx 1.33\right)$). Due to the large refractive index sensitivity of the (Au core)–(Ag shell) nanorods (~300 nm/RIU) [32], the large refractive index increment of 0.24 can lead to a plasmon redshift of ~70 nm. This calculated value is close to our experimental value (~86 nm). Note also that the plasmon resonance is broadened for nanorods conjugated with the PDMS substrate. We believe this is due to the additional plasmon damping induced by electron scattering at the interfaces between the nanorods and the PDMS matrix. Conjugation of the nanorods with the PDMS will introduce more interfaces between the nanorod and the PDMS matrix, which do not exist for nanorods deposited onto the glass substrate.

4-MBT molecules were utilized as probe molecules for evaluating the SERS activity of the prepared hybrid stretchable substrate. The 4-MBT molecules were able to form a well-defined monolayer on the surface of noble metals due to their thiol group [33]. Furthermore, they exhibit clear molecular fingerprints in 400–2000 cm$^{-1}$ on their Raman spectra. Both of these properties were crucial for precisely estimating the Raman enhancement factor (EF) of a SERS substrate. Figure 3(c) shows the comparison of the Raman spectra recorded from the 4-MBT molecules in powder form and adsorbed onto the hybrid substrate. The phenyl ring-breathing mode at 1080 cm$^{-1}$ (7a vibrational mode) and phenyl ring-stretching mode (8a vibrational mode) at 1595 cm$^{-1}$ can be clearly resolved in the two Raman spectra [34]. In addition, for molecules adsorbed onto the hybrid substrate, two more peaks, at 1378 and 1487 cm$^{-1}$, were observed. These two Raman bands are the intrinsic Raman modes of the 4-MBT molecules, which can be assigned to the in-plane phenyl ring vibrations [35]. Due to the very small Raman scattering cross sections of these two modes, they usually cannot be observed in ordinary Raman spectra collected from 4-MBT powder samples or solution samples [36]. However, if the molecules were adsorbed onto the (Au core)–(Ag shell) nanorods, the electric field enhancement induced by the plasmon resonance of the nanorods could strongly enhance the vibration amplitudes of these two Raman modes. As a result, they became active in the Raman spectra collected from the hybrid PDMS SERS substrate. Our finding is consistent with previous studies using Ag nanocubes [33, 35].

On the basis of the experimental measurements, we calculated the EF of the stretchable SERS substrate by referring to the 1595 cm$^{-1}$ mode using the following equation [34, 35]

$$\text{EF} = \frac{I_{\text{SERS}}/N_{\text{SERS}}}{I_{\text{Raman}}/N_{\text{Raman}}}$$

(1)

where $I_{\text{Raman}}$ and $I_{\text{SERS}}$ are the intensities of the 1595 cm$^{-1}$ band for the normal (measured on the 4-MBT powder) and SERS (measured on hybrid PDMS substrate adsorbed with the 4-MBT monolayer) spectra, $N_{\text{Raman}}$ is the number of molecules probed for a normal Raman scattering, and $N_{\text{SERS}}$ is the number of molecules probed on the SERS substrate, i.e. molecules adsorbed onto the (Au core)–(Ag shell) nanorods. In our calculations we employed the area intensity of the
1595 cm$^{-1}$ band for both $I_{\text{Raman}}$ and $I_{\text{SERS}}$. $N_{\text{Raman}}$ was estimated according to the focal volume of our Raman system ($V_{\text{f}} = 1.48$ pl). Specifically, $N_{\text{Raman}}$ equaled $V_{\text{f}} / V_{\text{M}}$. $V_{\text{M}}$ was the volume of an individual molecule, which was calculated according to the footprint (0.19 nm$^2$) and thickness (0.5 nm) of the molecules [35, 36]. For determining $N_{\text{SERS}}$, the 4-MBT molecules were approximated to be adsorbed as a monolayer onto the nanorods. Once the total surface area of the nanorods within a laser spot, $S$, was determined, $N_{\text{SERS}}$ could be obtained by dividing $S$ by the footprint of the molecule. $S$ could be calculated by timing the nanorod number with the surface area of an individual nanorod. The nanorod number within the laser spot was estimated according to the nanorod density and spot size of the incidence laser (diameter $\sim 1 \mu$m), which was $\sim 24$. We took into account all six facets of the nanorod, which caused an underestimation of the EF because for the hybrid substrate parts of the nanorods were immersed in the PDMS. These parts were not adsorbed with the molecules and therefore did not contribute to the EF. In calculating the surface area of an individual nanorod, it was modeled as a block with longitudinal and transverse lengths of 81 nm and 40 nm, respectively. Taking all these together, the EF was calculated to be $5.7 \times 10^7$, indicating an efficient Raman enhancement of the stretchable hybrid substrate. The EF was nearly one order of magnitude larger than those of the SERS substrates with Ag nanocubes [34, 35], which we believe was due to the larger electric field enhancements induced by the elongated (Au core)--(Ag shell) nanorods.

Figure 4. (a) Photograph showing the stretchability of the PDMS elastomer conjugated with (Au core)--(Ag shell) nanorods. (b) Photograph of the hysteresis-free translation stage employed for compressing the PDMS substrate. (c) Extinction spectra of the hybrid substrates in the normal state (black), under compression (red), and in the released state (green). (d) Raman spectra of the 4-MBT molecules adsorbed onto hybrid substrates in the normal state (black), under compression (red, spectrum upward shifted 500 counts), and in the released state (green, spectrum upward shifted 250 counts).

The hybrid substrate exhibited excellent malleability and can be bent back and forth without any breakdown (figure 4(a)). To demonstrate the tunability of the plasmonic resonances of the hybrid substrate, we employed a homemade hysteresis-free translation stage outfitted with a fine stepper (figure 4(b)). By placing the substrate between the two arms of the stage and screwing the stepper, compression or stretching force can be applied to the PDMS elastomer, whereby the hybrid PDMS substrate will undergo deformation. The applied force was kept small to avoid any bending or breakout of the PDMS. In such a manner, the conjugated (Au core)--(Ag shell) nanorods moved along with the deformation of the PDMS, and therefore the separations between different nanorods could be modulated accordingly (figure S4, supporting information). The plasmon wavelengths as well as oscillating strengths can then be tailored by taking advantage of the plasmon coupling effects. As shown in figure 4(c), for a stepper movement of 6.4 mm, the extinction maximum of the hybrid substrate was redshifted from 590 to 611 nm, which was close to the excitation laser (633 nm) during the Raman characterizations. In addition, the maximum intensity of the extinction intensity was also increased accordingly. The force applied to the hybrid PDMS substrate can be calculated according to the tension coefficient of the PDMS (22.7 mN m$^{-1}$) [37], which was 0.14 mN. Note that, in comparison with the spectrum shown in figure 3(b) (red curve) above, the plasmon resonance for the hybrid PDMS substrate before squeezing was blueshifted by $\sim 40$ nm. Such a discrepancy in the plasmon wavelength of the hybrid PDMS substrate is due to the different facilities used to obtain the spectra. The spectrum shown in figure 3(b) was measured by conventional UV/visible/near-infrared spectrophotometer (SHIMADZU). The spot size of the incidence light was about 5 mm. However, the spectrum shown in figure 4(c) was obtained using a microspectrophotometer (CRAIC Technology) with an incidence spot size of 1–2 $\mu$m. Due to the small inhomogeneous distribution of the nanorods onto the PDMS substrate (in terms of both the nanorod sizes and their separations), the extinction should vary at different locations of the sample. Measurements using a large spot size will show greater inhomogeneity. Therefore the spectra recorded using the conventional spectrophotometer and microspectrophotometer will be different, giving rise to the discrepancy between the spectra shown in figures 3(b) and 4(c) for the same hybrid PDMS substrate.
We then compared the Raman spectra of the 4-MBT molecules from the hybrid substrates at normal state and under compression. As shown in figure 4(d), the Raman bands between 1100 and 1600 cm$^{-1}$ of the 4-MBT molecules showed up when the substrate was compressed, whereas such bands could not be observed when the substrate was in its normal state. The increase of the intensity at the 1080 cm$^{-1}$ band is by about a factor of 1.5. This enhancement effect arose from bringing the plasmon wavelength of the substrate close to that of the incidence laser via compression. Note that the 1.5-times additional enhancement is lower than the expected value, which should be at least an order of magnitude higher. We believe that there are two reasons for this relatively low enhancement. First, previous studies have shown that the maximum enhancement of the Raman scattering intensity happens when the plasmon wavelength is located between the excitation laser wavelength and the vibrational shifted Raman wavelength [38, 39]. This phenomenon has been understood as resulting from a compromise between the excitation and emission enhancements. In our study, the plasmon wavelength of the flexible substrate after compression was 611 nm, which was at the blue side of the laser wavelength. Therefore the enhancement of the Stokes line of the 4-MBT molecules was not as large as expected. Another reason for the relatively low enhancement is that only the molecules located within the gaps between two nanorods, where the electromagnetic field enhancements are largest, can experience the additional enhancement from the plasmon coupling.

On the other hand, when the pressed substrate was released, the maximum extinction intensity was reduced to that of the substrate in the normal state (figure 4(c)). As a result, the Raman spectrum of the 4-MBT returned to that of the normal-state substrate (figure 4(d)). Note that for the released substrate the plasmon resonance was not blueshifted back to the original position. This discrepancy was probably due to the immersion of the nanorods in the PDMS during the compression process. When the nanorods were completely wrapped by the PDMS, their experienced refractive index was higher than that of the nanorods conjugated onto the original PDMS elastomer, where parts of the nanorod surfaces were exposed to air. It is very difficult for us to provide direct evidence for such speculation because characterization of the morphology of the nanorods conjugated onto the PDMS substrate is challenging. Currently we can only provide indirect evidence, by comparing the SEM images of the hybrid substrate after one cycle of compression and release. As shown in figure S5 (supporting information), in comparison with the image of the substrate at the initial state, the image for the released substrate exhibited a worse contrast and lower signal-to-noise ratio. This decline is caused by the decrease of the electrical conductivity of the hybrid substrate, which we believe is due to the immersion of the nanorods in the PDMS during the compression. In this circumstance, the exposed surface is pure insulating PDMS, giving rise to fewer backscattering electrons from the surface and therefore low image quality. Another piece of indirect evidence is the extinction spectrum of the flexible plasmonic substrate during another round of deformation. As shown in figure S6 (supporting information), the plasmon resonance showed redshift behavior with simultaneous enhanced extinction intensity when the substrate was compressed. When the substrate was released gradually, the extinction spectrum then recovered to that of the initial state. After the first cycle of compression and release, the nanorods were immersed in the PDMS and fixed by the matrix. Therefore in the following stretching cycle, the nanorods will not move within the PDMS, giving rise to the full recovery of the extinction spectrum after release.

We have also validated the universality of the SERS activity of the hybrid PDMS substrate by using different types of probing molecules. For these measurements, the substrates were carefully immersed in the dye solutions with various...
molecular concentrations. We prolonged the incubation period to guarantee the uniform adsorption of the dyes onto the substrates. After the incubation the substrates were taken out of the dye solutions and washed carefully using ethanol to remove excess molecules that were not adsorbed onto the substrates. A 633 nm laser was utilized as the excitation source. The Raman spectra of rhodamine 6G (R6G) and methylene blue (MB) molecules with different concentrations adsorbed on the hybrid substrate are shown in figures 5(a) and (b). The molecular concentrations were varied from $1 \times 10^{-7}$ to $1 \times 10^{-13}$ M for both R6G and MB. The Raman spectra collected from the molecules adsorbed onto the blank PDMS substrate were also given for reference, which showed no Raman bands at the highest molecular concentrations. On the contrary, the hybrid PDMS substrate exhibited excellent Raman enhancements for both molecules, where characteristic Raman bands can even persist when the molecular concentrations are as low as $1 \times 10^{-13}$ M. On the basis of these measurements, we constructed the calibration curves of the SERS intensity depending on the molecular concentrations of R6G and MB, respectively (figure S7, supporting information). For the R6G and MB molecules, the calibrations were done according to the Raman mode at 1648 cm$^{-1}$ and 1626 cm$^{-1}$, respectively. Raman spectra of molecules adsorbed onto the blank PDMS substrate with $10^{-7}$ M were employed as the reference. The calibrations were referred to the quantity $R$, which was defined by dividing the Raman intensity of various molecular concentrations by the reference. From the calibration curves, one can judge that the detection limits of the hybrid PDMS SERS substrate for R6G and MB molecules are $1 \times 10^{-13}$ M. Such a high Raman sensitivity is even better than those of some SERS substrates proposed in recent studies, where large-area aligned Ag nanowire films or periodic structured Ag-nanoparticle films were utilized [40, 41].

4. Conclusions

In summary, we have proposed a highly stretchable hybrid substrate composed of PDMS elastomer conjugated with (Au core)–(Ag shell) nanorods. By compressing via external mechanical force to reduce the separation between the nanorods, the Raman enhancement factor can be increased. It is worth noting that the fast tunable SERS active performance shown here cannot be easily achieved by conventional materials. We believe that the proposed hybrid substrate can pave the way for the design and fabrication of flexible and tunable platforms for surface-enhanced spectroscopies that will be widely utilized in future medical and biological sensing technologies.

Acknowledgments

The authors thank Professor Baojun Li from Sun Yat-sen University for his assistance in microspectrometer measurements. We also thank Mr Lin Liu from the Instrumental Analysis and Research Center of Sun Yat-sen University for conducting the TEM measurements. This work was financially supported by the National Natural Science Foundation of China (Grant Nos 11474364 and 51202300), the Guangdong Natural Science Funds for Distinguished Young Scholars (Grant No 2014A030306017), the Doctoral Fund of the Ministry of Education of China (Grant No 20120171120012), the Program for Changjiang Scholars and Innovative Research Team in University (Grant No IRT13042), and the Fundamental Research Funds for the Central Universities.

References

[1] Yumi A, Youngjun J, Donghwa L and Youngu L 2015 Copper nanowire–graphene core–shell nanostructure for highly stable transparent conducting electrodes ACS Nano 9 3125–33
[2] Dong T, Zhou Y, Hu D-G, Xiao P, Wang Q, Wang J, Pei J and Cao Y 2015 Free-standing, flexible, multifunctional, and environmentally stable superhydrophobic composite film made of self-assembled organic micro/super-nanostructures through solution process J. Colloid Interface Sci. 445 213–8
[3] Lin H-J, Li L, Ren J, Cai Z-B, Qiu L-B, Yang Z-B and Peng H-S 2013 Conducting polymer composite film incorporated with aligned carbon nanotubes for transparent, flexible and efficient supercapacitor Sci. Rep. 3 1353
[4] Singh J P, Chu H Y, Abell J, Tripp R A and Zhao Y-P 2012 Flexible and mechanical strain resistant large area SERS active substrates Nanoscale 4 3410–4
[5] Chiang Y-L, Chen C-W, Wang C-H, Hsieh C-Y, Chen Y-T, Shih H-Y and Chen Y-F 2010 Mechanically tunable surface plasmon resonance based on gold nanoparticles and elastic membrane polydimethylsiloxane composite Appl. Phys. Lett. 96 041904
[6] Robinson A M, Zhao L-L, Shah Alam M Y, Bhandari P, Harron S G, Dedukuri D, Blackburn J and Brosseau C L 2015 The development of ‘fab-chips’ as low-cost, sensitive surface-enhanced Raman spectroscopy (SERS) substrates for analytical applications Analyst 140 779–85
[7] Galzarano S, Loseu V, Gravina R, Giannantonio R, Sgroi M, Jafari R and Fortino G 2011 From modeling to implementation of virtual sensors in body sensor networks IEEE J. Sens. 12 583–93
[8] Yan L, Lee S, Kim Y-S and Yoo H-J 2010 A 5.2 mW self-configured wearable ROey sensor network concentrator and a $12 \mu W$ wirelessly powered sensor for a continuous health monitoring system IEEE J. Solid-State Circuits 45 178–88
[9] Yang H and Robert F 2008 Wireless body sensor networks for health-monitoring applications Physiol. Meas. 29 R27–56
[10] Veronika S, Ivana Š, Martina N and Blanka V 2015 SERS microRaman spectral probing of adsorbate-containing, liquid-overlayed nanosponge Ag aggregates assembled from fractal aggregates J. Raman Spectrosc. 10 1002
[11] Gabudean A M, Biro D and Astilean S 2012 Hybrid plasmonic platforms based on silica-encapsulated gold nanorods as effective spectroscopic enhancers for Raman and fluorescence spectroscopy Nanotechnology 23 485706
[12] Ye J, Wen F, Sobhani H, Lassiter J B, Dorpe P V, Nordlander P and Halas N J 2012 Plasmonic nanocusters: near field properties of the Fano resonance interrogated with SERS Nano Lett. 12 1660–7
[13] Liu M, Tian Q, Li Y-L, You B, Xu A and Deng Z-X 2015 Activation of the solid silica layer of aerosol-based C/SiO$_2$ particles for preparation of various functional multi-shelled hollow microspheres ACS Langmuir 31 5164–73
[14] Meyer S A, Le Ru E C and Etcheogin P G 2011 Combining surface plasmon resonance (SPR) spectroscopy with surface-enhanced Raman scattering (SERS) Anal. Chem. 83 2337–44
[15] Xie W and Schlücker S 2014 Rationally designed multifunctional plasmonic nanostructures for surface-enhanced Raman spectroscopy: a review Rep. Prog. Phys. 77 116502
[16] Yang Y, Zhong X-L, Zhang Q, Blackstad L G, Fu Z-W, Li Z-Y and Qin D 2014 The role of etching in the formation of Ag nanoplates with straight, curved and wavy edges and comparison of their SERS properties Small 10 1430–7
[17] Meneghetti M, Scaris A, Litti L, Marcelongo G, Amendola V, Gobbo M, Chio M D, Boscaini A, Fracasso G and Colombatti M 2012 Plasmonic nanostructures for SERRS multiplexed identification of tumor-associated antigens Small 8 3733–8
[18] Jiang Y, Wu X-D, Shan G-Y, Li J-H, Chen Y-W, Zhang X-T and Liu Y-C 2015 The effect of Au nanoshells with controllable aggregation on SERS enhancement Mater. Res. Express 2 045004
[19] Daedu L and Sangwoon Y 2015 Gold nanocube-nanosphere dimers: preparation, plasmon coupling, and surface-enhanced Raman scattering J. Phys. Chem. C 119 7873–82
[20] Chen J, Feng S-L, Gao F, Edward G, Xu J, Wang S, Huang Q and Lu X-N 2015 Fabrication of SERS-active substrates using silver nanofilm-coated porous anodic aluminum oxide for detection of antibiotics J. Food Sci. 80 834–40
[21] Zhu X-L, Shi L, Liu X-H, Zi J and Wang Z-L 2010 A mechanically tunable plasmonic structure composed of a monolayer array of metal-capped colloidal spheres on an elastomeric substrate Nano Res. 3 807–12
[22] Malynych J, Robuck H and Chumanov G 2001 Fabrication of two-dimensional assemblies of Ag nanoparticles and nanocavities in poly(dimethylsiloxane) resin Nano Lett. 1 647–9
[23] Zdyrko B, Kinnan M K, Chumanov G and Luzinov I 2008 Fabrication of optically active flexible polymer films with embedded chain-like arrays of silver nanospheres Chem. Commun. 11 1284–6
[24] Yang Y, Shi J-L, Kawanura G and Nogami M 2008 Preparation of Au-Ag, Ag-Au core–shell bimetalllic nanoparticles for surface-enhanced Raman scattering Scr. Mater. 58 862–5
[25] Jiang R-B, Chen H-J, Shao L, Li Q and Wang J-F 2012 Unraveling the evolution and nature of the plasmons in (Au Core)–(Ag Shell) nanorods Adv. Opt. Mater. 24 200–7
[26] Nikoobakhht B and El-Sayed M A 2003 Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method Chem. Mater. 15 1957–62
[27] Gole A and Murphy C J 2004 Seed-mediated synthesis of gold nanorods: role of the size and nature of the seed Chem. Mater. 16 3633–40
[28] Ke S-L, Kan C-X, Mo B, Cong B and Zhu J-J 2012 Research progress on the optical properties of gold nanorods Acta Phys. Chim. Sinica. 28 1275–90
[29] Okuno Y, Nishioka K, Kiya A, Nakashima N, Ishibashi A and Niidome Y 2010 Uniform and controllable preparation of Au–Ag core–shell nanorods using anisotropic silver shell formation on gold nanorods Nanoscale 2 1489–93
[30] Lu G, Li H and Zhang H 2012 Gold-nanoparticle-embedded polydimethylsiloxane elastomers for highly sensitive Raman detection Small 8 1336–40
[31] Shao L, Ruan Q F, Jiang R B and Wang J F 2014 Macroscale colloidal noble metal nanocrystal arrays and their refractive index-based sensing characteristics Small 10 802–11
[32] Lee Y H, Chen H J, Xu Q-H and Wang J F 2011 Refractive index sensitivities of noble metal nanocrystals: the effects of multiplarm plasmon resonances and the metal type J. Phys. Chem. C 115 7997–8004
[33] Camargo P H C, Ryenga M, Au L and Xia Y 2009 Isolating and probing the hot spot formed between two silver nanocubes Angew. Chem. Int. Ed. 48 2180–4
[34] Li W, Camargo P H C, Lu X and Xia Y 2009 Dimers of silver nanospheres: facile synthesis and their use as hot spots for surface-enhanced Raman scattering Nano Lett. 9 485–90
[35] Camargo P H C, Au L, Ryenga M, Li W and Xia Y 2010 Measuring the SERS enhancement factors of dimers with different structures constructed from silver nanocubes Chem. Phys. Lett. 484 304–8
[36] Khan M A, Hogan T P and Shanker B 2008 Surface-enhanced Raman scattering from gold-coated germanium oxide nanowires J. Raman Spectrosc. 39 893–900
[37] She H, Chaudhury M K and Owen M J 2000 Silicones and silicone-modified materials ACS Symp. Series 729 241
[38] Haynes C L and Van Duyne R P 2003 Plasmon-sampled surface-enhanced Raman excitation spectroscopy J. Phys. Chem. B 107 7426–33
[39] Willets K A and Van Duyne R P 2007 Localized surface plasmon resonance spectroscopy and sensing Annu. Rev. Phys. Chem. 58 267–97
[40] Zhou W P, Hu A M, Bai S, Ma Y and Bridges D 2015 Anisotropic optical properties of large-scale aligned silver nanowire films via controlled coffee ring effects RSC Adv. 5 39103–9
[41] Bai S, Zhou W P, Lin Y H, Zhao Y, Chen T, Hu A M and Duley W W 2014 Ultraviolet pulsed laser interference lithography and application of periodic structured Ag-nanoparticle films for surface-enhanced Raman spectroscopy J. Nanopart. Res. 16 2470