Tunable platforms by coupling gold nanorectangles and pNIPAM for surface-enhanced Raman scattering

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Abstract
This paper describes a new plasmonic platform made of lithographic gold nanorectangles array coated by a thermosensitive polymer layer poly(N-isopropylacrylamide). This polymer layer responds to temperature variations by conformational changes and is therefore able to vary the distance between the gold surface and the molecular probes. Hence, this stimulable substrate can be used as a tunable device for surface-enhanced Raman scattering (SERS) using Nile blue A as a molecular probe. We show that an increase of the external temperature reversibly induces a significant enhancement of the Nile blue A SERS signal. This was attributed to a stronger interaction between the gold nanorectangles and Nile blue A. The thermosensitive plasmonic devices developed in this paper thus provide a dynamic SERS platform for sensing application.

Keywords: gold nanorectangles, plasmonic, thermoresponsive polymer, pNIPAM, SERS
Classification numbers: 2.02, 2.09, 5.00, 5.04, 5.10, 5.13

1. Introduction
Since its discovery in 1977 surface-enhanced Raman scattering (SERS) is a powerful vibrational spectroscopic technique for ultrasensitive analyzing the composition of materials (solids, liquids and gases) without special preparation of the sample [1–3]. The SERS technique allows to strongly increase the Raman signals of molecules adsorbed onto plasmonic (gold, silver...) nanostructured surfaces [4–6]. The aggregates formation is requisite to receive strongly active areas where the electromagnetic field is enormous due to the interaction of interparticle plasmon [7]. However, aggregation causes heterogeneous surfaces with the random distribution in density and shape of the hot spots. Thus, the quantitative detection is impossible. To solve this issue, two-dimensional (2D) substrates of plasmonic nanostructures were fabricated. Recent reports described the 2D structures based on silver nanoparticles on silicon for trace detection of the paraquat [8, 9]. However, the size of the particles and the distance between them were not uniform. Another report developed 2D arrays of gold nanodots by sputtering Au using anodic aluminum oxide template which can control the size of particles and the distance between them [10]. In our study we produced lithographic gold nanostructures, which have uniform size, shape and density. One of the requirements to receive strong SERS relies on the analytes because SERS signals are strong in the first-layer. Hence, analysts that have good affinity toward the gold surface lead to high SERS signals. However, the analytes with low or no affinity commonly do not have SERS effect [7]. To solve this issue, gold nanostructures have been grafted with various materials that can attract the analyte close to the gold surface or increase the analyte concentration [11, 12]. Poly-N-isopropylacrylamide (pNIPAM) coating has the capacity...
of trapping efficiently hydrophobic analytes close to the gold surface, leading to the enhancement of their Raman signal [13, 14].

In this work a stimulable device is designed by lithographic gold nanorectangles (AuNRs) array coated with a thermoresponsive pNIPAM. This polymer has the ability to change the distance between the gold nanorectangles surface and the molecular probes. We used pNIPAM as a spacer due to its phase transition behaviour. Indeed, pNIPAM brush is swollen and become hydrophilic state in water at the temperature below the lower critical solution temperature (LCST ~ 32 °C). Above the LCST, pNIPAM brush is collapsed hydrophobic state [15]. These conformational changes from the swollen state to the collapsed state of pNIPAM are expected to modify the properties of the substrate as a function of temperature and thus modify the trapping functionality to the substrate of the molecular probes.

2. Experiment

2.1. Chemicals

N-isopropylacrylamide monomer (NIPAM) 99% and N,N,N′,N′′,N′′-pentamethyldiethyltriamine (PMDETA) were purchased from Acros Organics. Triethylamine (TEA) 99% was purchased from Sigma Aldrich. 2-bromoiso- butyryl bromide 97% was bought from Alfa Aesar. 2-(4-amino-phenyl)ethanol 98%, CuBr 98%, and nile blue were purchased from Sigma Aldrich. 2-bromoisobutyryl bromide 97% was bought from Alfa Aesar. The ATRP reaction was carried out in deionized water containing 0.1 M 2-bromoisobutyryl bromide and 0.12 M tert-butyl nitrite 90% was purchased from Merck. Tert-butyl nitrite 90% was purchased from Merck. Tert-butyl nitrite 90% was purchased from Merck. Tert-butyl nitrite 90% was purchased from Merck. Tert-butyl nitrite 90% was purchased from Merck.

2.2. Gold nanorectangles functionalization by pNIPAM

The lithographic gold nanorectangles (AuNRs) array produced by electron-beam lithography (EBL) was grafted pNIPAM by following the multi-steps strategy relying on three major steps (figure 1): (i) the grafting of the aryl group derived from 4-hydroxyethylbenzene diazonium tetrafluoroborate salt, termed HEBDT (+N2–C6H4–CH2–CH2–OH) was chemically synthesized following the approach described in our previous report [16].

2.3. Instrumentation

The extinction spectra were recorded by the LOT ORIEL spectrometer model MS 260i, combined with an optical microscope (OLYMPUS BX 51). Tapping-mode atomic force microscopy (AFM) of the samples before and after the modification was performed using SPM Nanoscope III (Veeco, Bruker) set-up in water. The SERS spectra were measured on a Jobin-Yvon LABRAM HR 800 Raman micro spectrometer with the excitation laser at 632.8 nm.

3. Results and discussion

3.1. Characterization of AuNR@pNIPAM array

Recent efforts have been focused on identifying appropriate nanoplasmonic materials which have sensitive spectra plasmon upon a variation of the local environment. Wherein, AuNRs are interesting materials due to their optical properties with the plasmon wavelength that can be finely tuned by modification of AuNRs aspect ratio. Therefore, we focused our attention on AuNRs which have unique optical properties with two localized surface plasmon (LSP) bands. The longitudinal and transversal LSP band corresponds to the oscillation of the electrons parallel to the major and the short axis, respectively. AuNRs remain popular for plasmonic applications due to the adjustable ability of the LSP resonance wavelength by varying the aspect ratio, defined as the long axis (length) divided by the short axis (width) of a rod-shaped particle, their strong scattering efficiency and a small LSP damping.

In this work we consider an AuNRs array with a small aspect ratio r = 1.2 (200 nm long, 167 nm wide and 30 nm high). The AFM images of these AuNRs are shown in figure 2(a). The extinction band around 596 nm corresponds to the transversal LSP mode (black dashed line in figure 2(c)). The other extinction band occurs at higher wavelengths around 616 nm corresponding to the longitudinal LSP mode (black dashed line in figure 2(d)). For such anisotropic particles, a strong red-shift is expected when the refractive index changes. The surrounding medium of AuNRs is changed by grafting the polymer film. The AFM images of AuNRs array before and after polymer grafting show that the pNIPAM brushes are grafted only on the AuNRs and not on the substrate (figures 2(a) and (b)). The dry polymer thickness in the air was \( L_{dry} \sim 5 \) nm. The presence of polymer layer on the AuNRs leads to the location of peak absorption red-shift in wavelength of LSP due to an increase of refractive index: \( \Delta L_{sp} = 31 \) nm for the transversal LSP mode, and \( \Delta L_{sp} = 41 \) nm for the longitudinal LSP mode (figures 2(c) and (d)).

The dynamic swelling ratio (\( \alpha \)) of pNIPAM was determined as \( \alpha = L_{swollen}/L_{dry} \) (where \( L_{swollen} \) and \( L_{dry} \) are the thickness of pNIPAM brush at swelling and dry states, respectively). The swelling ratio was deduced from our report to \( \alpha \sim 2 [17] \). Thus, the pNIPAM thickness in the swollen state can be deduced to \( L_{swollen} \sim 10 \pm 2 \) nm. When the AuNRs are deoxidized and heated above the LCST, the pNIPAM brush is collapsed and become hydrophobic, and thus the substrate was taken out of the flask and carefully washed with water and ethanol. Finally, the substrate was dried under the argon flush.
were coated by pNIPAM, the phase transition of the polymer can change the refractive index of the surrounding medium of the AuNRs and lead to the optical properties of plasmonic nanostructures modified. The pNIPAM thickness can decrease from 10 to 5 nm and the refractive index can increase from 1.37 to 1.43 by raising the temperature [18]. In order to characterize the thermosensitive properties of this system, we considered its optical response as a function of temperature. The longitudinal mode of AuNRs is highly sensitive in wavelength to the local environment. Thus, in optical studies, the longitudinal LSP mode of AuNRs has received main attention. Extinction spectra on the longitudinal LSP mode of the AuNR@pNIPAM sample recorded in water at 20 and 40 °C are shown in figure 3(a). From these spectra, it is clear that red-shift of the LSPR band is observed ∼ 4 nm upon an increase of the temperature, due to a change in the medium index in vicinity of AuNRs by the conformational change of the pNIPAM. The LSP red-shift as a function of temperature is plotted in figure 3(b). The sigmoidal curve fitting (red solid line) based on the experimental data (black dot) showed a sharp transition between two plateau areas below and above the LCST of pNIPAM.

3.2. SERS activities of AuNR@pNIPAM substrate

The SERS activity based on the synthesized hybrid substrate was determined by Nile blue A (NBA) dye as a probed molecule. Firstly, the substrate was immersed in NBA 0.73 ppb solution for 5 min. Next, it was washed with water and ethanol, and then dried. The temperature dependence of the SERS

![Figure 1. Multi-steps strategy of functionalization of AuNRs by pNIPAM.](image1)

![Figure 2. The AFM images of AuNRs before (a) and after (b) pNIPAM grafting. (c) Transversal extinction spectra recorded in the air of AuNRs array before (black dashed line) and after pNIPAM grafting (red line). (d) Longitudinal extinction spectra recorded in the air of AuNRs array before (black dashed line) and after pNIPAM grafting (red line).](image2)
The activity of AuNR@pNIPAM substrate was investigated by measurement their Raman spectra below and above the LCST of pNIPAM. SERS spectra of NBA recorded in water at 20 and 40 °C were shown in figure 4. The enhanced Raman signals of NBA probe were characterized by bands from C–C–C and C–N–C deformations at 498 cm⁻¹ and 591 cm⁻¹, C–C–C and N–C–C in-plane bending at 665 cm⁻¹, C–H bending at 1256 and 1186 cm⁻¹; and ring stretching vibrations at 1643, 1542, 1493, 1435, 1419 and 1357 cm⁻¹. The bands are agreed upon by the literature [19].

Recently, the sensitivity studies of several types of SERS substrates based on silver/gold nanostructures on 2D substrates demonstrated that the detection limit can be down to 0.01 ppm for parquat [8, 9] and 1 ppb for methamidophos [10]. In our report, hybrid substrate based on lithographic gold nanorod arrays and pNIPAM presents a high sensitivity which allows to detecting the NBA molecules at ultra-low concentration (0.73 ppb). Attentively, the results demonstrate an increase of the SERS response of NBA molecules at the temperature above the LCST of pNIPAM (compared to the SERS spectra registered below the LCST). The band intensities increase up to three-fold. This can be explained by an increase of the local field intensity when the distance between the AuNRs surface and the analyte is decreasing. Hence, the distance between the AuNRs surface and the molecular probes have influence on the SERS signal. It is due to the pNIPAM conformation change upon the temperature variation. Interestingly, figure 4 shows that SERS signal decreases back to the first spectra recorded at 20 °C when cooling down the substrate to below the LCST (20 °C). Especially, the modifications of the Raman signal intensity of NBA obtained for AuNR@pNIPAM substrate are fully reversible upon the variation of external temperature.
The temperature dependence of the intensity variation of Raman band at 1181 cm$^{-1}$ was plotted in figure 5. A steep increase was observed when the temperature increases from 28 to 34 °C corresponding to the phase transition zone of pNIPAM. It is remarkable that this thermo-driven variation was fully reversible during repeating cycles of the temperature decrease from 40 and 20 °C. Interestingly, the intersection between two curves with increasing and decreasing temperatures is located around 32 °C, the LCST of pNIPAM. The full reversibility of the system indicates that our thermoresponsive system allows us to dynamically tune the distance between the AuNRs surface and analyte.

4. Conclusions

In conclusion, an interesting hybrid nanostructure consisting of thermoresponsive pNIPAM and AuNRs array was successfully fabricated. By our strategy of functionalization, the polymer thickness can be easily estimated by AFM. The synthesized hybrid plasmonic nanostructure was used as a platform for trace detection of Nile blue A by Raman spectroscopy. A high SERS effect was observed on the AuNR@pNIPAM substrate. On the other hand, the results demonstrated that the SERS signal can be dynamically and reversely tuned as a function of temperature. Above the transition phase temperature of pNIPAM, the hybrid substrate produced an enormous SERS signal because of the collapse of polymer brushes lead to decrease of the distance between probe molecule and gold surface. Our obtained results in this works demonstrate the huge promising of stimulable polymer-coated nanostructures as effective devices for sensing applications.

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