Self-assembly of monodisperse composite microgels with bimetallic nanorods as core and PNIPAM as shell into close-packed monolayers and SERS efficiency

Xu Dong a,b,⁎, Siyuan Chen b, Jian Zhou b, Liying Wang b, Liusheng Zha b,⁎⁎

a State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecule Science, Fudan University, Shanghai 200433, PR China
b State Key Laboratory of Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, PR China

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In this study, monolayer film of composite microgels with bimetallic nanorods as core and PNIPAM as shell (Au@AgNR@PNIPAM) assembly on a modified surface of silicon wafer was formed by a dip coating method. The effects of temperature, pH and concentration of KCI on the surface morphology of monolayer were discussed. And when the temperature was 50 °C; pH value was 4.0; concentration of KCI was 10 mM, a monolayer film would be formed much better. By the characterization of atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM), the monolayer structure of Au@AgNR@PNIPAM composite microgels assembled products was confirmed. The analysis of attenuated total reflection Fourier transform infrared absorption spectrum (ATR-FTIR) confirmed that the chemical composition of monolayer film on the silicon wafer surface was PNIPAM. And the UV-visible spectroscopy showed Au@AgNR in the monolayer film still maintained their LSPR optical performance. Assembled product has high stability, the surface morphology and coverage of the monolayer film did not change significantly when testing in a swing speed of 100 rpm Rocking Shaker within 30 min. The assembled monolayer was used as SERS substrates to trace the 10⁻¹ M to 10⁻⁴ M 1-naphthol in aqueous solution, and the analysis results was with good reproducibility.

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1. Introduction

Intelligent microgels are usually in the form of colloid particles dispersed in water, if assembling it into fibers, a monolayer film, multilayer film, colloidal crystals or hydrogel, the generated smart materials or devices with macroscopic dimensions will present some unique properties, which will further broaden the application range of composite microgels [1]. As a common thermo-responsive microgel, intelligent microgels based on poly(N-isopropylacrylamide) (PNIPAM) have caused most studies in the past years, which included the research attention in assembly [2]. In addition, intelligent microgels based on PNIPAM prepared by precipitation polymerization has a good monodispersity, which would be helpful for PNIPAM microgels assembled into a product with two-dimensional (2D) or three-dimensional (3D) structure [3]. A new kind of hollow hydrogel microfiber with discontinuous hollow structure was prepared using an ice-segregation-induced self-assembly process by Liu et al. [4]. They synthesized monodisperse thermo-responsive hollow PNIPAM microgels by seed precipitation polymerization using colloidal SiO2 nanoparticles as seeds first, and then removing the silica cores of the formed SiO2/ PNIPAM core/shell composite microgels with hydrofluoric acid. Finally, the discontinuously hollow hydrogel microfibers were produced by unidirectional freezing of 1 wt.% hollow PNIPAM microgel aqueous dispersion in liquid nitrogen bath, followed by freeze-drying to remove the formed ice crystals. In 1999, monodisperse PNIPAM microgels were assembled into colloidal crystals for the first time by Sneff and Richtering et al. [5]. However, due to its unstability, these colloidal crystals have little practical value. Its structure can be easily damaged by external stimuli such as mechanical disturbances. In order to stabilize the structure of colloidal crystals, Hu et al. added a crosslinking agent in the colloidal crystals to form chemical bond between microgel particles [6]. In recent years, assembly of composite microgels based on PNIPAM has also been reported. Suzuki et al. presented the assembly of colloidal crystals composed of various thermoresponsive core/shell microgels and their hybrid microgel counterparts that contain localized Au nanoparticles [7]. To obtain colloidal crystals, they conducted a three-stage polymerization. First, core microgels composed of cross-linked PNIPAM were synthesized by precipitation polymerization. Using these microgels as cores or “seeds”, a copolymer shell of PNIPAM was added to these core particles using a functional comonomer. Finally, a second shell consisting solely of cross-linked PNIPAM was added onto the preformed
core/shell microgels by using this seeded polymerization technique. The three-dimensional colloidal crystals were obtained by centrifugation and thermal annealing. Recently, Karg et al. [8] showed the preparation of nanocrystal superlattices assembled from gold-poly-N-isopropylacrylamide core-shell particles and the characterization of their fascinating diffraction behavior by means of UV-vis spectroscopy. These nanocrystal superlattices exhibited pronounced diffraction in the visible (440–560 nm) with peak half-widths of the order of 10 nm. And the position of the Bragg peak was simply tuned by adjusting the particle volume fraction.

There are three common methods to assemble microgels on a specific substrate to form a monolayer film [1]. Dip coating is a method that immersed the substrate in an aqueous dispersion of PNIPAM microgels for a moment and then removed [9]. There is no requirement for the size and shape of substrate in the dip coating process, so the applicability of this method is very strong. Compared with the dip coating method, a spin coating method have a capability of producing microgels monolayer film faster, but this method requires the substrate has smooth surface and limited size, while need a specific orientation coating apparatus [10]. Drip coating is a method that dripping the diluted microgel dispersion on a substrate, followed by drying in air, the capillary action between the particles promoted the microgel orderly arranged in a monolayer film [11]. However, the distance between microgels of the monolayer film prepared by this method is larger and the surface coverage is smaller.

To our best knowledge, the close-packed monolayer film of Au@AgNR@PNIPAM composite microgels assembled on a silicon wafer has not been reported so far. It is well known that the AuNRs exhibit higher SERS activity than the corresponding spherical ones owing to the so-called lightning-rod effect [12]. The performance of AgNRs coated on preformed AuNRs in enhancing Raman signals has been found to be much better than that of the AuNRs of the same size [13]. However, when they used as SERS substrate only the analytes containing thiol or amino group have SERS signal strong enough for detection of their minute amounts, because the two kinds of functional groups have strong affinity towards metal surfaces [14]. Although their suitable surface modification can increase their affinity with other analytes, such as polycyclic aromatic compounds or organic acids or bases, the modifying moiety provides strong SERS signals that overlap and screen those corresponding to the analyte [15]. Therefore, to further expand the range of applications of Au@AgNR@PNIPAM composite microgels, and improve the homogeneity and reproducibility of SERS substrates, the close-packed monolayer film of Au@AgNR@PNIPAM composite microgels assembled on a silicon wafer was prepared by dip coating method. The surface morphology, chemical composition and optical performance were identified using atomic force microscope (AFM), scanning electron microscopy (SEM), Fourier transform infrared attenuated total reflection absorption spectroscopy (ATR-FTIR) and UV-3600 UV-vis spectrophotometer, respectively. The effect of the temperature, pH and concentration of KCl on the surface coverage and roughness was intensively investigated. The stability of the obtained monolayer film was also discussed. Ultimately, the close-packed monolayer film of Au@AgNR@PNIPAM composite microgels was used as the SERS substrates for detecting SERS signal of 1-naphthol in aqueous solution.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPAM, 95%) was purified by repeated recrystallization from n-hexane/benzene (v/v:40/60) mixed solvent. N, N’-methylene bisacrylamide (MBA, 95%), 2, 2’-azobisis(2-amidinopropane hydrochloride) (AAPH, 98%) and butenoic acid (BA, 96%) were used as purchased from Aldrich. N/P-type of 111/100 double-sided polished silicon wafers were purchased from the Shanghai Sijie Optical Materials Co., Ltd. Toluene, acetone, concentrated sulfuric acid (H2SO4, 98%), hydrogen peroxide (H2O2, 30%) and potassium chloride were all analytical grade chemical reagents. All deionized water used in the synthesis and characterization was made using a Millipore Direct-Q system.

2.2. Synthesis of monodisperse Au@AgNR@PNIPAM complex microgels

Monodisperse bimetallic nanorods with gold (Au) nanorod core and silver (Ag) shell (Au@AgNRs) were synthesized through seed-mediated growth process by reduction of AgNO3 using Au nanorods with narrow size and shape distribution as seeds [16]. Then, the Au@AgNRs were encapsulated by crosslinked PNIPAM to produce thermo-responsive Au@AgNR@PNIPAM composite microgel with well-defined core-shell structure by seed-precipitation polymerization method using BA modified Au@AgNRs as seeds [17].

2.3. Preparation of close-packed monolayers on a silicon wafer

The process of Au@AgNR@PNIPAM composite microgels assembled on a silicon wafer to form a monolayer film is schematically depicted in Fig. 1. The substrates used were silicon wafers, which prior to use, were cleaned in ultrasonic followed by toluene, acetone, deionized water 2 min to remove organic residues from the surface. After drying, the silicon wafers were subjected to prolonged exposure to 450 W power electron-beam bombardment 100 s using the HD-1 A type of cold plasma treatment apparatus (Changzhou Zhongke Changtai Plasma Processing Apparatus Plasma Technology Co., Ltd.). And then, the silicon wafers were dipped into H2SO4/H2O2 (v/v:7/3) solution at 100 °C for 60 min, and finally rinsed several times with deionized water and placed in a vacuum oven at 80 °C for 24 h. All these procedures lead to oxidation of the silicon surface to give a thin native silicon oxide layer. In water (pH = 4), the silicon wafer is negatively charged.

The positive charged microgel particles were then adsorbed onto this treated silicon wafer. Prior to adsorption the temperature of the microparticle dispersion (1.5 wt.% in 10 mM KCl solution) was raised to 50 °C, and this was then left to equilibrate for 15 min, allowing the microgel particles to adopt their deswollen state. The precoated silicon wafer was dipped into this microparticle dispersion, at 50 °C, for 30 min to allow maximum coating of the substrate surface to occur. The silicon wafer was then transferred to water, at room temperature, for a further 12 h, to remove the extra microgels. Then, the microgel-coated wafer was allowed to dry in a clean air environment. Close-packed monolayer on a modified silicon wafer of Au@AgNR@PNIPAM composite microgels was fabricated.

2.4. Characterization

Atomic force microscopy (AFM) (NanoScope IV, US Veeco) was employed to characterize the morphology and to estimate the coverage of the dried Au@AgNR@PNIPAM complex microgels adsorbed on the silicon wafer. The AFM imaging was performed with a multimode (nanoscope IV) from Veeco in air using a tapered Si-cantilever (nanosensors, PPP-NCHR-50) with a tip radius smaller than 10 nm. The roughness of the monolayer film surface could be attained from these AFM images, usually using root mean square roughness (Rms/nm) to represent. The AFM images were also used to calculate the coverage of the monolayer film on the surface of silicon wafer. The coverage of the monolayer film is expressed here in terms of particle density on the surface, define as the number of microgels per unit area (μm2).

Scanning electron microscopy (SEM) was used to estimate the morphology of the adsorbed microgel monolayer. SEM micrographs were obtained using a HITACHI S-4800 field emission instrument. In addition, the semi-quantitative analysis of the elements of oxygen on the silicon surface before and after treatment was determined by X-ray energy dispersive spectroscopy (EDS) (Quantax, Germany Bruker) associated with SEM. The surface zeta potential of the Au@AgNR@PNIPAM complex microgels aqueous dispersion with pH = 4 at 20 °C and 50 °C.
respectively, was verified by zeta potential analyzer (Zetasizer Nano-ZS, Britain MALVERN). Fourier transform infrared attenuated total reflection absorption spectroscopy (ATR-FTIR) (Nicolet 6700, US Thermo Fisher) was utilized to analyze the chemical composition of the surface monolayer. The ATR-FTIR spectra were measured on the wave number range from 400 to 4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

Ultraviolet-visible (UV-vis) spectroscopy was applied to study the plasmonic property of Au@AgNR in the composite microgels. The UV–vis spectra of microgel monolayer on the silicon surface were recorded in the wavelength range of 300 to 1100 nm at room temperature on a UV–3600 uv-vis spectrophotometer (Japan SHIMADZU). The stability of the microgel monolayer on the silicon surface was tested by oscillator (KS260Basic, Germany IKA) in a swing speed of 100 rpm Rocking Shaker within 30 min. An inVia-Reflex micro-Raman spectroscopy system (Renishaw, UK) with a 633 nm solid laser source of 50 mW power was used to evaluate the SERS activity and Raman signal reproducibility of close-packed monolayer film of Au@AgNR@PNIPAM composite microgels as substrate using 1-naphthol as analyte. Its microscope attachment was based on an Olympus system with a 50× long-distance objective.

3. Results and discussion

AFM images of the surface of the untreated silicon wafer (a) and treated silicon wafer (b) were shown in Fig. S1 in the supporting information, which exhibits that the treated silicon wafer has a smooth and clean surface, and the surface roughness is 0.8 nm. However, the surface of the untreated silicon wafer is non uniform, and the surface roughness is 4.3 nm. This means that after treatment the organic residues were removed from the surface. Fig. S2 shows the EDS spectrograms of the untreated silicon wafer (a) and treated silicon wafer (b). It can be found from these spectrograms that the content of oxygen of the silicon wafer before and after treatment are 0.72% and 0.87%, respectively, indicating that the the Si-OH was formed after the oxidation treatment on the surface of silicon wafer. Further verification of the existence of the hydroxyl on the surface of the silicon wafer was obtained by the change of the contact angle of the surface. Fig. S3 shows the outside view of droplets on the surface of the untreated silicon wafer (a) and treated silicon wafer (b). As we can see, the contact angle of the surface of silicon wafer before and after treatment are 74°and 46°, respectively, which means the hydrophilicity of the surface is significantly enhanced after treatment.

Due to the 2,2’-azobis (2-amidinopropane hydrochloride) (AAPH) was used as the initiator in the preparation of Au@AgNR@PNIPAM composite microgels, the initiator was decomposed into amidino with positive charge and then connected on the surface of the microgel, as schematically shown in Fig. S4. In the pH = 4.0 environment, the potential of the surface of the composite microgels at 20 °C is +2.1 mV measured by zeta potential instrument, showing that the composite microgels have positive charge. As the temperature raised to 50 °C, the potential of the surface increases to +19.7 mV, indicating that volume contraction leads to charge quantity of the surface increases. Therefore, when the silicon wafer with negative charge was dipped into Au@AgNR@PNIPAM microgel composite aqueous dispersion, microgel particles was adsorbed on the surface of silicon wafer through electrostatic interactions to assemble a monolayer film. In addition, the charge density of the surface of composite microgels is also related to the pH and electrolyte concentration of the aqueous dispersion. Hence, the influence of the temperature, pH and electrolyte concentration on the assembly of close-packed monolayer was discussed in this paper.

Fig. 2 shows the changes of coverage and RMS roughness of the surface of silicon wafer which Au@AgNR@PNIPAM composite microgels were assembled on with different temperatures (a), pH (b) and KCl concentration (c), respectively. As we can see from Fig. 2 (a), as the temperature of the aqueous dispersion is raised from 20 °C to 50 °C, the coverage of the composite microgels on the silicon wafer increases from 4 to 14 and the surface roughness decreases from 7.6 nm to
4.7 nm, indicating the formation of the monolayer film surface more smooth. When the temperature up to 35 °C, there are sharp changes of coverage and surface roughness, possibly due to the volume phase transition of the composite microgels. The charge density of the surface increases along with the contraction of microgel volume in response to temperature changes [18]. Thus, the Au@AgNR@PNIPAM complex microgels have low surface charge density at 20 °C, and only a small amount of microgels adsorb on the immersed silicon surface. As the temperature rises, volume phase transition of composite microgels occurs and the surface charge density increases, adsorbed microgels on the silicon surface will be more. These AFM images of monolayer that assembled at different temperatures are shown in Fig. S5 in the Supporting information, which reveals that the Au@AgNR@PNIPAM complex microgels adsorb on the silicon surface at 50 °C in a collapsed state.

Fig. 2 (b) illustrates the changes of surface coverage and RMS roughness of silicon wafer which Au@AgNR@PNIPAM composite microgels were assembled on in aqueous dispersion at different pH. As the pH is increased from 3.0 to 9.0, their surface coverage are decreased from 16 to 1, meanwhile their surface roughness increased from 4.6 to 9.2. From the AFM images under the condition of different pH, as shown in Fig. S6 in the Supporting information, number of composite microgels absorb on the silicon surface are sharp increased within the pH ≤ 4. This phenomenon may be reflected in two aspects. On the one hand, the pH value has an effect on the dissociation degree of the hydroxyl groups on the silicon wafer (Si-OH → Si-O⁻ + H⁺) and affects the charge density of the wafer surface. As has reported, Isoelectric point of Si-OH is between 2 and 3 [19], so when the pH > 4, the impact of pH on the charge density of silicon surface is less. On the other hand, the pH value has an effect on the charge density of the surface of Au@AgNR@PNIPAM composite microgels. Bao et al. [18] utilized 2, 2′-azobis (2 - amidinopropane hydrochloride) (AAPH) as initiator to prepare temperature-sensitive poly(N-isopropylacrylamide) (PNIPAM) microgels by precipitation polymerization under various reaction pH conditions. The pH dependence of surface charge density of the microgels with amidino groups on their surfaces was evidenced by the variation of their zeta potentials as a function of pH and found the zeta potential of the microgel is positive. When the pH value of the aqueous medium decreased from 12.0 to 4.0, the charge density is gradually increased and up to the maximum at pH = 4.0, which is similar to the surface coverage tendency in the Fig. 2 (b). Small changes occur in surface coverage when pH < 4 and further evidence that electrostatic interactions is the main driving force of Au@AgNR@PNIPAM complex microgels adsorbed on the silicon surface to form monolayer film.

Since, the surface of Au@AgNR@PNIPAM complex microgels have same charge, there may exist electrostatic repulsion between them which will cause difficulty to adsorb on the wafer surface tightly. In order to weaken the electrostatic repulsion between the microgels, expecting to obtain a more close-packed microgel monolayer film, we try to join a KCl electrolyte solution in the aqueous dispersion, to have certain shielding effect on the surface charge of the microgels. The relationship between surface coverage and roughness and the KCl concentration is shown in Fig. 2 (c) and its AFM images are exhibited in Fig. S7. With increasing the KCl concentration, their surface coverage remarkably changes from 13 to 20, and surface roughness changes from 4.1 to 3.2 nm correspondingly, proving that the arrangement of the microgels on the silicon surface increasingly dense and the monolayer surface becomes more smoothly.

Close-packed monolayer of Au@AgNR@PNIPAM composite microgels on the modified silicon wafer was assembled. While T = 50 °C, pH = 4 and C_{KCl} = 10 mmol/L, the monolayer film on the silicon surface has higher surface coverage and lower surface roughness. The AFM images of the obtained monolayer film are shown in Fig. 3, and the thereby measured surface coverage and roughness are 21 and
3.1 nm, respectively. It can be found from Fig. 3 that monolayer film with close-packed structure and flat surface can be easily prepared under these conditions.

In addition, the FE-SEM images of the prepared monolayer film in top view (a) and side view (b) in Fig. 4 further confirm the monolayer structure of the assembly product. The SEM images of the obtained...
monolayer film, as shown in Fig. 4(a), exhibit that they have close-packed structure with illegible contact interface between microgels. FE-SEM test is processed under high vacuum conditions, the microgels in a collapsed state, however the Au@AgNR can not be collapsed and present convex state. Therefore, it can be clearly observed that Au@AgNRs in the monolayer film have substantially equal distance, and thereby calculated the distance between Au@AgNRs, is 142 nm. The surface coverage is twenty-two composite microgels per square micron, consistent with the results of Fig. 3, revealing that the assembled film is monolayer. Meanwhile, this result is also indirect evidence that the monolayer film on the silicon surface has high stability. Under high vacuum conditions, the composite microgels do not move from the silicon surface. The side view of the monolayer film is shown in Fig. 4(b), in which the monolayer structure is obviously observable and the Au@AgNR@PNIPAM composite microgels on the surface of silicon wafer is closed-packed.

In order to confirm the chemical constituents of the monolayer film on the silicon surface, the comparation between PNIPAM microgels and monolayer film was confirmed by ATR-FTIR results, as illustrated in Fig. S8. Fig. S8 (a) and (b) are the FTIR spectrums of PNIPAM microgels and monolayer film of Au@AgNR@PNIPAM composite microgels, respectively. Although the two spectra are overall very similar, a small blue shift of amide I and II bands (1636 cm\(^{-1}\) and 1526 cm\(^{-1}\)) of PNIPAM chain appear in the spectrum of the composite microgels on the silicon surface. The interaction between the nitrogen atoms of the amide groups of PNIPAM and the Ag shell of the Au@AgNRs may result in a blue shift of the bands ascribed to the amide groups in the FTIR spectrum [20].

The UV-vis spectra of Au@AgNR@PNIPAM composite microgels in diluted aqueous dispersion (a) and monolayer film of Au@AgNR@PNIPAM composite microgels assembled on the surface of silicon wafer (b) are shown in Fig. 5. It can be found from Fig. 5 that the plasmonic peaks of monolayer film on the silicon surface are as narrow as that of Au@AgNR@PNIPAM composite microgels in diluted aqueous dispersion, proving that assembly does not change the optical properties of Au@AgNRs in the composite microgels. After assembling, the longitudinal plasmonic peak (719 nm) is notably red-shifted, whereas the transverse plasmonic peak (510 nm) blue-shifting is not remarkable. The longitudinal wavelength red-shift of Au@AgNR@PNIPAM microgels on the silicon surface is only attributed to the local refractive index increase around the Au@AgNR resulting from water expelling during their temperature induced volume phase transition [21]. Thus, the shrinking state when the process of assembly was carried out at 50 °C should be the key factor for blue-shifting of their longitudinal plasmonic bands. Moreover, the monolayer film on the silicon surface characterized by UV-vis spectra is in a dry state.

It is necessary to assess the stability of the monolayer film on the silicon surface, in order to develop the applications of monolayer film of Au@AgNR@PNIPAM composite microgels. The surface appearance of the monolayer film on the silicon surface after different times shaking was observed by AFM. The AFM images of the monolayer after enduring the Rocking Shaker at speed of 100 rpm and different times are exhibited in Fig. 6. As illustrated in Fig. 6, the morphology and surface coverage of the monolayer film have little change after shaking 30 min. A small part of Au@AgNR@PNIPAM composite microgels fell off from the wafer surface after shaking 60 min and a lot of microgels are still adsorbed on the silicon surface even after shaking 120 min. This means the monolayer film assembled by dip coating method at 50 °C has a good stability. Both the static electricity interactions between the positively charged microgel and the negatively charged silicon wafer and the entanglement between the polymer chains of composite microgels are contributed to it. It was found that surface of PNIPAM microgels prepared by precipitation polymerization had a hair-like structure [22]. The Au@AgNR@PNIPAM composite microgels assemble a close-packed film on the silicon surface at 50 °C. When the temperature return to room temperature, hair-like polymer chains in the surface
of microgels will be an extended state, and it is possible for “miscible” and cause mutual entanglement.

The SERS activity of close-packed monolayer film of Au@AgNR@PNIPAM composite microgels on a modified silicon wafer used as SERS substrates was evaluated by recording spectra of 1-napthol, which has no ability to absorbed on Au@AgNRs, as well as hard to be detected by common detection method [23]. And two approaches were utilized to evaluate the reproducibility of the SERS signals. Firstly, the monolayer film was used as the substrate to measure the SERS spectra of different concentrations of 1-napthol solution from $10^{-5}$ M to $10^{-1}$ M, and the results are given in Fig. 7. The spectra were obtained by averaging five readings at the point of each sample. With the increase of 1-napthol concentration, its SERS intensity is progressively raised. The plot of the intensity of the 1447 cm$^{-1}$ peak in the SERS spectra versus 1-napthol concentrations is illustrated in Fig. S9, which can be fitted into the line with a correlation coefficient of 0.96 ($n = 5$). This result shows that

Fig. 6. AFM images of the monolayer after enduring the Rocking Shaker at speed of 100 rpm and different times.
there is a good linear relationship between the SERS intensity and the analyte concentration, indicating that the SERS signal based on monolayer film of Au@AgNR®PNIPAM composite microgels as substrates is highly reproducible. Second, ten times of SERS measurements were carried out with the same $1 \times 10^{-5}$ M 1-naphthol aqueous solution as analyte. Fig. 8 shows the SERS spectra of these measurements, and the RSD of the intensities of their 1447 cm$^{-1}$ peaks is 2.6%. This result further reveals that the SERS signals based on monolayer film of Au@AgNR®PNIPAM composite microgels as substrates are of high reproducibility. No doubt, the high SERS signal reproducibility should arise from the monodisperse distribution of Au@AgNR®PNIPAM composite microgels and close-packed structure on the silicon surface.

4. Conclusions

In summary, close-packed monolayer film of Au@AgNR®PNIPAM complex microgels assembly on a modified surface of silicon wafer was formed by a dip coating method, and the surface morphology of monolayer is able to be affected by temperature, pH and concentration of KCl. AFM and FE-SEM results confirm that the Au@AgNR®PNIPAM composite microgels assembled on the surface of silicon wafer has a monolayer structure. The ATR-FTIR spectrum results confirm that the chemical composition of monolayer film on the silicon wafer surface was PNIPAM. The UV-visible spectroscopy results indicate that the monolayer film still maintained the LSPR optical performance of Au@AgNRs. The monolayer film assembled by dip coating method has a good stability. When the assembled monolayer was used as SERS substrates for probing 1-naphthol, the obtained Raman signals are highly reproducible.

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Appendix A. Supplementary data

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