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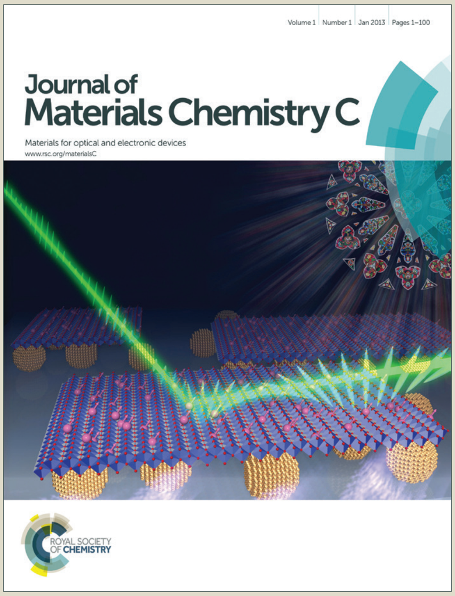

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Temperature and pH tunable plasmonic property and SERS efficiency of the silver nanoparticles within the dual stimuli responsive microgels

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The silver nanoparticles (AgNPs) loading microgels with interpenetrating polymer network structure composed of separately crosslinked poly(acrylic acid) and poly(N-isopropylacrylamide) were prepared through in-situ reduction reaction of silver ions coordinated into their networks. The temperature or pH dependent hydrodynamic diameters measured using dynamic laser light scattering show that the produced hybrid microgels have pH and temperature dual stimuliresponsive property with little mutual interference between the temperature and pH responsive components. The localized surface plasmon resonance wavelength of the AgNPs inside the microgels can be reversibly tuned with temperature changing from 20℃ to 45℃ or pH value changing from 3.0 to 7.0. When the hybrid microgels were used as the surface enhanced Raman scattering (SERS) substrates for probing minute amount of 4-mercapto benzoic acid in aqueous solution, its SERS intensity is remarkably increased with pH value lowing from 7.0 to 3.0 or temperature rising from 20℃ to 45℃.If the two stimuli are simultaneously exerted, the SERS intensity is greatly elevated. The temperature and pH value measuring results show that the hybrid microgels are able to be utilized as SERS microsensors for measuring both pH value and temperature of their surroundings.

Introduction

Compared to other metal nanoparticles, silver nanoparticles (AgNPs) have dominant plasmonic optical property due to their very high extinction coefficient.[1,2] The coupling between the oscillating electromagnetic fields on their surfaces originating from plasmon resonance provides huge enhancement of the local electromagnetic fields and makes the noble metal nanoparticles powerful for plasmonic sensing.[3] Furthermore, the greatly strong surface electromagnetic fields resulting from the coupling make AgNPs very efficient in their use as substrate for surface enhanced Raman scattering (SERS) sensing.[4] If AgNPs are loaded into stimulus responsive colloidal microgels with the particle size of 10~1000 nm, their plasmonic property and surface electromagnetic field enhancement effectcan be tuned by external stimulus thanks to the stimulus induced variation of their surrounding refractive index and distances[5]. On the other hand, external stimulus can be sensed by detecting variation of their properties.[6,7] In addition, the self-aggregation and oxidation of AgNPs can be avoided due to their immobilization within the microgels' polymer networks.[8] Moreover, the formed hybrid microgels have the advantages similar to smart microgels, such as tunable dimensions, fast responsiveness, desirable colloidal stability and potential biocompatibility.[9] Hence, AgNPs loading stimulus-responsive hybrid microgels have potential applications in microsensor, smart microreactor, drug delivery and controlled release, medical diagnosis, etc.[10, 11]

It is known that temperature and pH are two important environmental factors in biomedical and chemical systems.[12] For example, the temperatures at some disease sites (e.g. inflammation sites) within human body are usually higher than that at normal sites. The pH values within the body differ in different tissues and cellular compartments, such as those in the gastrointestinal tract. Most tumor tissues as well as inflamedor wound tissues exhibit a pH that differs from the 7.4 value found in normal tissue.[13] Therefore, temperature or pH stimulus responsive polymer materials attract much attention over the past decade.[14] When noble metal nanoparticles were loaded into temperature or pH responsive microgels, their plasmonic property and surface electromagnetic field enhancement effect can be tuned by temperature or pH, respectively.[15~17] The produced hybrid microgels have potential application in the mobile plasmonic or SERS microsensor for detecting environmental temperature or pH variation.[18] For instance, Kawaguchi et al. utilized N-isopropylacrylamide and glycidylmethacrylate copolymerized microgels as templates for in situ synthesis of Au@Ag core/shell bimetallic nanoparticles, and the produced hybrid microgels can be used as microsensors for probing environmental temperature change through colorimetric assay based on their localize surface plasmon resonance (LSPR) wavelength variation.[19] In our group, AgNPs were loaded into the super pH responsive microgels by in situ reduction of Ag^+ coordinatedinto their polymer network. The LSPR property and SERS efficiency of the AgNPs inside the formed hybrid microgels was found to be pronouncedly dependent on environmental pH value within the range from 4.0 to 6.0. They have attractive potential application in pH probing mobile plasmonic or SERS microsensors.[16] To our best knowledge, the noble metal nanoparticles loading hybrid microgels used as microsensors for detecting both temperature and pH change have never been reported so far.

In this paper, in order to fabricate the mobile SERS microsensors for detecting both temperature and pH change, AgNPs were loaded into the microgels with interpenetrating polymer network (IPN) structure composed of separately crosslinked poly(N-isopropylacrylamide) (PNIPAM) and poly(acrylic acid) (PAA) (PNIPAM/PAA IPN microgels) by in-situ reduction of Ag^+ coordinated into their polymer networks. Their plasmonic property determined by ultraviolet-visible spectroscopy was found to be pronouncedly dependent on environmental pH value within the range from 3.0 to 7.0 and temperature within the range from 20℃ to 50℃. When the hybrid microgels were used as SERS substrates for detecting minute amount of 4-mercapto benzoic acid in aqueous solution, their SERS efficiency can be modulated by pH or temperature. The hybrid microgels can be utilized as SERS microsensors for measuring both pH value and temperature of their surroundings with little mutual interference between temperature and pH responsive components.

Experimental section

Materials

N-Isopropylacrylamide (NIPAM) (purity 95%, Acros.) was purified by recrystallization from a mixture of toluene and hexane (60:40, V/V). N,N'-methylenebisacrylamide (MBA) (purity 95%, Aldrich) was purified by recrystallization from methanol. Acrylic acid (AA) (purity 99.5 %, Acros) was purified by distillation under reduced pressure to remove hydroquinone inhibitor. Sodium dodecyl sulfate (SDS) (analytical grade, Shanghai Chemical Reagent Co.), *N,N,N',N'*-tetramethylethylenediamine (TEMED) (purity 98％, Acros）, potassium persulfate (KPS) (analytical grade, Shanghai Chemical Reagent Co.), sodium borohydride ($NaBH_4$) (purity 95%) and silver nitrate ($AgNO_3$) (purity 99.8%) were all used as received. All deionized water used in the synthesis and characterization was made using a Millipore Direct-Q system.

Preparation of AgNPs/(PNIPAM/PAA IPN) hybrid microgels

PNIPAM/PAA IPN microgels were firstly synthesized according to the reference.[20] Typically, 3.80 g NIPAM, 0.078 g MBA and 0.024 g SDS were dissolved in 240 mL of deionized water and stirred under nitrogen flow for 1 h to remove dissolved oxygen. After the solution was heated to 70℃, 0.16 g of KPS dissolved in 20mL of water was then added, and the polymerization was allowed to proceed for 4 h at 70℃ under continuous nitrogen flow. Then, 15 mL of the produced PNIPAM microgel dispersion was diluted 10 times with deionized water, and 0.97 gAA and 0.22 g MBA were added. Finally, 0.08 g KPS and 0.08 g TEMED separately dissolved in 5 mL of deionized water were added successively to the dispersion, and the polymerization reaction was conducted at 21℃ for 1.5 h under nitrogen atmosphere. The resultant PNIPAM/PAA IPN microgels were purified by three times of centrifugation and dispersion in deionized water, and then freeze dried to produce a powder sample.

AgNPs/(PNIPAM/PAA IPN) hybrid microgels were then prepared by in-situ reduction of Ag^+ ions coordinated into PNIPAM/PAA IPN microgels by $NaBH_4$. Typically, 0.05 g of freeze dried PNIPAM/PAA IPN microgels was dispersed in 97 mL deionied water, and the pH value of the formed dispersion was adjusted to 8.0 by 0.1 mol/L NaOH solution. Then, certain amount of $AgNO_3$ was dissolved in the dispersion, followed by stirring and purging with nitrogen gas for 30 min at 30℃. Subsequently, certain amount of $NaBH_4$ dissolved in 3 mL water was added into the reaction solution, and the reduction reaction was carried out at 30℃under nitrogen purge for 1 h. The obtained brown dispersion was centrifugated at 6000 rpm for 18 min and then redispersed in deionized water to remove the reactant and the produced free AgNPs. Changing the used amounts of $AgNO_3$ and $NaBH_4$, a series of AgNPs/(PNIPAM/ PAA IPN) hybrid microgels were prepared, as shown in Table 1.

Table 1 Recipe for preparing AgNPs/(PNIPAM/PAA IPN) microgels and the weight contents and average diameters of the AgNPs within the microgels

Sample	Amount of $AgNO_3$ (g)	Amount of $NaBH_4$ (g)	Weight content of AgNPs (%)	Average diameter of AgNPs (nm)
IPN-Ag-1	0.01	0.01	14.2	11.6±1.0
IPN-Ag-2	0.02	0.02	21.2	13.2±0.8
IPN-Ag-3	0.03	0.03	38.5	14.3±0.7

Characterization of AgNPs/(PNIPAM/PAA IPN) hybrid microgels

Transmission electron microscopy (TEM) images were taken with a 2100F transmission electron microscope (JOEL, Japan) at a voltage of 200 kV. Diluted microgel dispersions were dropped onto carbon coated copper grids and dried at room temperature. The average diameters of the AgNPs within the hybrid microgels were statistically obtained by measuring the diameters of 100 particles on the TEM images by particle size analysis software. Thermal gravimetric analysis (TGA) was carried out on a TGA-7 analyzer (Perkin–Elmer, USA). After drying under vacuum at room temperature for about 24 h, the samples were heated in the range of 30-800℃with a heating rate of 10°C/min in N_2 purge. The hydrodynamic diameters (D_H) of the hybrid microgels dispersed in the waters of various pH values were measured via BI-200SM dynamic light scattering (DLS) (Brookheaven, USA), which is equipped with a solid laser source (wavelength of 532 nm and output power of 100 mW) and a BI-9000AT digital autocorrelator. The scattering light was collected at 90°, and the CONTIN statistical method was used to convert the measured correlation data into a particle size distribution. The measurement temperature was controlled with a thermostated naphthane bath, and the highly diluted microgels dispersion was allowed to equilibrate thermally for at least 15 min before each set of measurements.

Plasmonic property measurements

The ultraviolet-visible absorption spectra at varied pH values were obtained from a Lambda 35 ultraviolet-visible spectrometer with a Peltier temperature controller (UV-vis) (Perkin-Elmer, USA). A quartz cuvette with 1 cm optical path length was used. The pH values of AgNPs/(PNIPAM/PAA IPN) microgels dispersion diluted to 0.05 wt% concentration was adjusted by 0.1 mol/L HCl or NaOH aqueous solution.

SERS measurements

The surface-enhanced Raman spectra (SERS) were measured on an inVia-Reflex micro-Raman system (Renishaw, UK) equipped with a multi-channel charge-coupled device (CCD) detector and a confocal microscope (DM2500 M, Leica) upon excitation by 633 nm laser line. All the SERS spectra were the results of 10 s accumulations. The sample was placed in a THMS600 temperature controllable cell (Linkam, USA) and equilibrated thermally for at least 30 min before SERS measurement.

Results and discussion

Fabrication and characterization of AgNPs/(PNIPAM/PAA IPN) hybrid microgels

AgNPs/(PNIPAM/PAA IPN) hybrid microgels were fabricated by in situ reduction of Ag^+ ions coordinated into PNIPAM/PAA IPN microgels at pH 8.0, as schematically illustrated in Fig.1. Since the pK_a of PAA polymer is ca. 4.25, the -COOH groups within PNIPAM/PAA IPN microgels are mostly dissociated into $-COO^-$ groups under pH=8.0. After addition of $AgNO_3$, Ag^+ ions can diffuse into the swollen microgels and coordinate with negatively charged -COO$^-$ groups, leading to their homogenous distribution within the microgels network. Subsequently followed by addition of $NaBH_4$, the coordinated Ag^+ ions were reduced into Ag atoms, and the neighboring Ag atoms aggregated and generated AgNPs. The Ag atoms on AgNPs can interact with the -COO$^-$ groups of PAA component or the amide groups of PNIPAM component,[16] so the AgNPs are immobilized within the polymer network to produce stable AgNPs/(PNIPAM/PAA IPN) hybrid microgels.

The TGA results of the obtained AgNPs/(PNIPAM/PAA IPN) hybrid microgels are exhibited in Table 1, the weight content of their embedded AgNPs can top 38.5%. As the used amounts of $AgNO_3$ and $NaBH_4$ are increased, the AgNPs content inside the microgels is elevated, due to reduction of more Ag^+ ions by $NaBH_4$ and generation of increasing Ag atoms. This fact can be visualized by their appearances, as show in Fig.S1 in the Supporting Information. As their AgNPs content is raised, the color of AgNPs/(PNIPAM/PAA IPN) hybrid microgels dispersions with identical concentration is gradually darkened. The TEM images of AgNPs/(PNIPAM/PAA IPN) hybrid microgels with different AgNPs contents are shown in Fig.2 (a), (b) and (c), respectively. As is clear from the images, the AgNPs are homogeneously distributed within the hybrid microgels, and their number within one microgel is notably increased with their weight content. Fig.2 (d) is the typical high resolution TEM image of the AgNPs within the hybrid microgels. It can be found from this image that the AgNPs approximately exhibit spherical shape, with relatively well monodispersity. As listed in Table 1, the average diameters of the loaded AgNPs measured from the TEM images are within the range of 11 to 15 nm, which are increased with the used amount of $AgNO_3$ and $NaBH_4$.

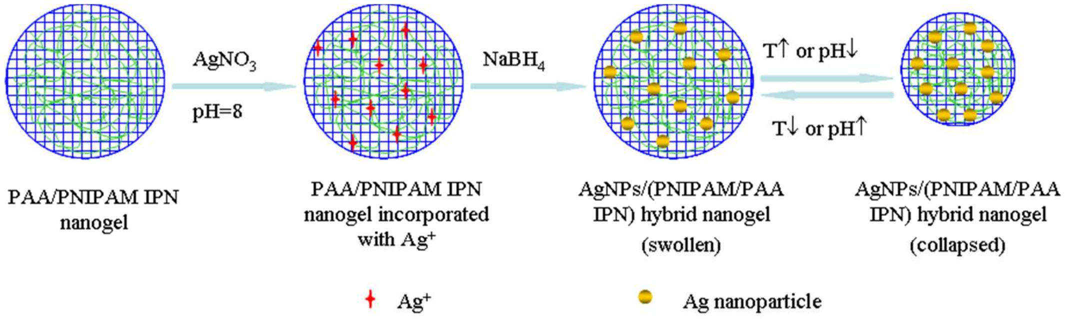

Fig. 1 Schematic of fabricating AgNPs/(PNIPAM/PAA IPN) hybrid microgels and their pH/temperature dual responsiveness.

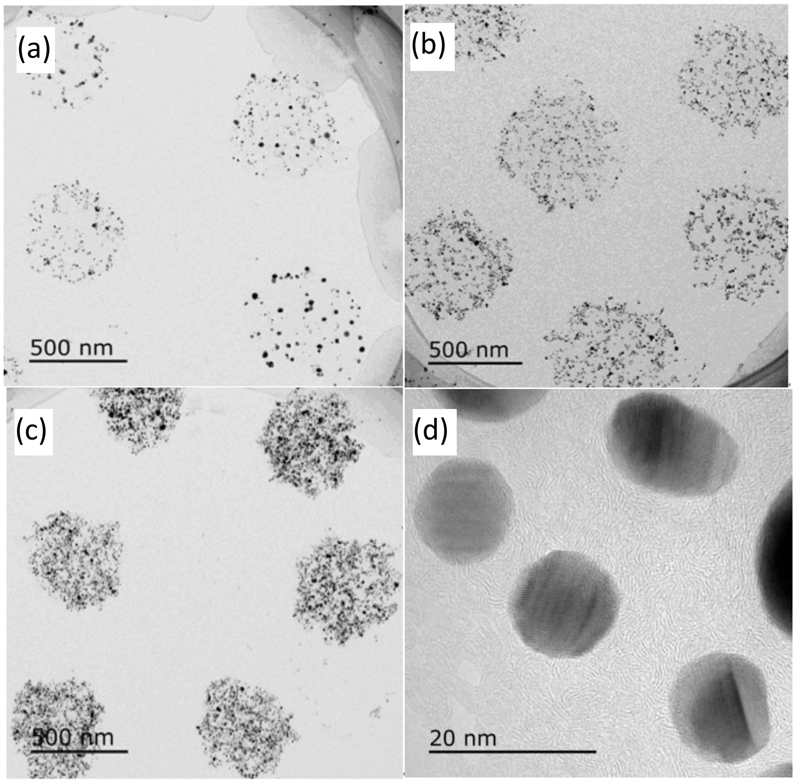

Fig. 2 TEM images of AgNPs/(PNIPAM/PAA IPN) hybrid microgels((a):IPN-Ag-1; (b): IPN-Ag-2; (c): IPN-Ag-3)) and (d) typical TEM image of AgNPs inside the microgels.

Temperature or pH triggered volume phase transition behavior of AgNPs/(PNIPAM/PAA IPN) hybrid microgels

The hydrodynamic diameters of AgNPs/(PNIPAM/PAA IPN) hybrid microgels with different AgNPs contents at 20℃ or 40℃ as a function of the pH value of their dispersion medium are shown in Fig.3 (a) and (b), respectively. Whether at 20℃ or 40℃, as the pH value rises from 4.0 to 6.0, their particle sizes increase sharply, indicating that AgNPs/(PNIPAM/PAA IPN) hybrid microgels have marked pH responsiveness. When the pH value is lower than the pK_a of the -COOH groups of PAA component, the hydrogen bonding interactions between the groups and the amide groups of PNIPAM component result in shrinking of the hybrid microgels. As the pH value rises above their pK_a, the –COOH groups are gradually dissociated into $-COO^-$ groups, leading to swelling of the microgels due to the increased osmotic pressure and electrostatic repulsion between the charged groups.[20] However, as their AgNPs content is elevated, the pH responsiveness of AgNPs/(PNIPAM/PAA IPN) hybrid microgels is weakening. This is possibly because of the fact that the interaction between AgNPs and the PAA or PNIPAM component acts as the crosslinking point inside the microgels, resulting in reduction of their volume change magnitude after pH triggering phase transition.

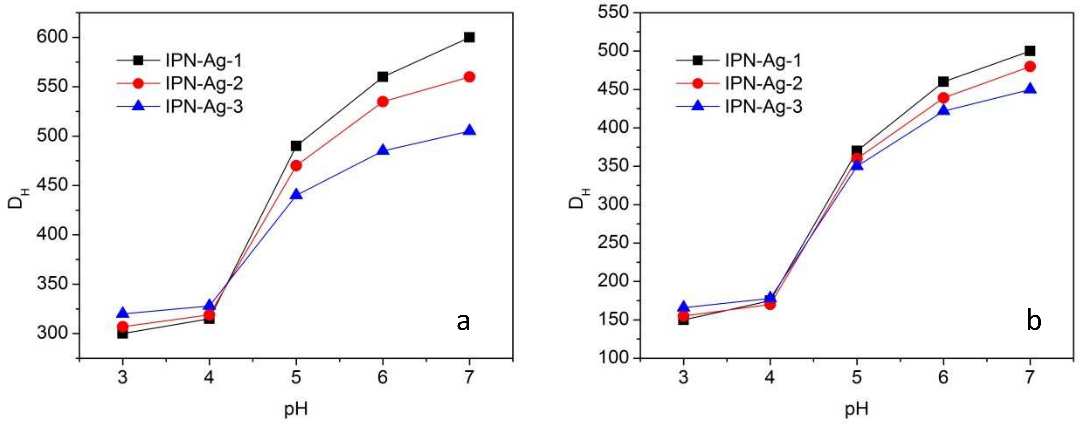

Fig.3 pH dependent hydrodynamic diameters (D_H) of AgNPs/(PNIPAM/PAA IPN) hybrid microgels at the temperature of 20℃(a) or 40℃ (b).

The temperature dependent hydrodynamic diameters (D_H) of AgNPs/(PNIPAM/PAA IPN) hybrid microgels with different AgNPs content at pH 3.0 or 7.0 are shown in Fig. 4 (a) and (b), respectively. Under two pH conditions, their particle sizes lower significantly as the temperature is raised from 25 ℃ to 40℃, indicating that they have remarkable temperature responsiveness. Even if the -COOH groups of the PAA moiety are disassociated into -COO^- ones at pH 7.0, their hydrodynamic diameters can undergo 50 to 100 nm change, which implies that the pH responsive component (PAA) has little interference with their temperature induced volume phase transition. At pH 3.0, their temperature responsiveness is hardly dependent on their AgNPs content. However, at pH 7.0, it is pronouncedly lessened with increasing their AgNPs content. This further confirms that the interaction between the AgNPs and the -COO^- groups is present inside AgNPs/(PNIPAM/PAA IPN) hybrid microgels, which acts as crosslinking points and weakens their swelling extent upon temperature triggered volume phase transition.

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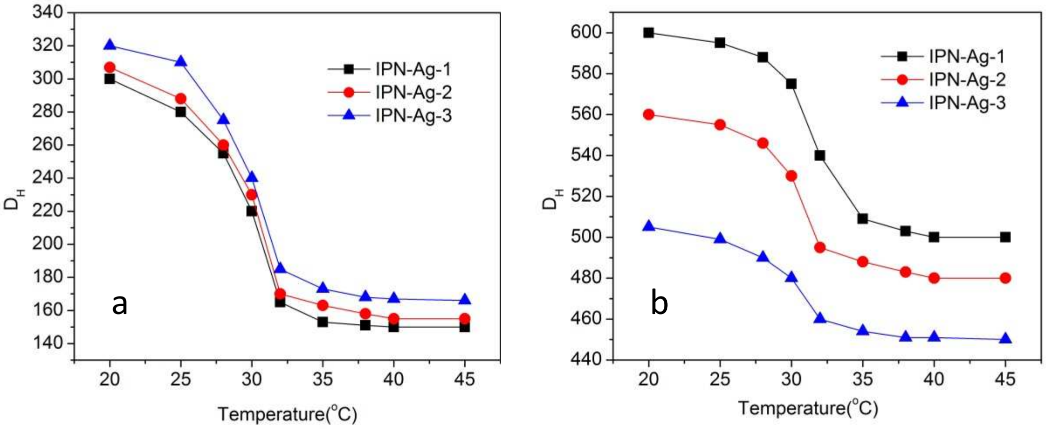

Fig. 4 Temperature dependent hydrodynamic diameters (D_H) of AgNPs/(PNIPAM/PAA IPN) hybrid microgels at the pH value of 3.0 (a) or 7.0 (b).

pH and temperature tunable plasmonic property of AgNPs/(PNIPAM/PAA IPN) hybrid microgels

The pH or temperature dependent plasmonic property of the AgNPs within AgNPs/(PNIPAM/PAA IPN) hybrid microgels was studied by UV-vis spectroscopy at two different temperatures (20℃ and 40℃) or two pH values (7.0 and 3.0), respectively. The UV-vis spectra of AgNPs/(PNIPAM/PAA IPN) hybrid microgels with different AgNPs contents at various pH values under the temperature of 20℃ or 40℃ are illustrated in Fig. 5. At both temperatures, the absorption band at ca. 425 nm is present for all the hybrid microgels within the pH range from 3.0 to 7.0. Their maximum absorption wavelengths (λ_{max}), i.e. LSPR wavelength of the AgNPs inside the microgels, are redshifted with pH value lowering, indicating that the plasmonic property of the AgNPs can be tuned by pH. The higher the AgNPs content within the microgels, the larger their LSPR wavelength redshifting magnitude within the same pH range at identical temperature. This result exhibits that the tunability of the AgNPs' plasmonic property by pH is increased with their content inside the microgels. The plots between the λ_{max} and pH value at the two temperatures for all AgNPs/(PNIPAM/PAA IPN) hybrid microgels are illustrated in Fig. S2. It can be found that the LSPR wavelength of the AgNPs is drastically redshifted within the pH range from 4.0 to 5.0, in agreement with the pH range of their particle size change (as shown in Fig.3). This may be due to two reasons. One is refractive index increase around the AgNPs inside the hybrid microgels thanks to expelling of a large amount of water during their pH decrease induced volume phase transition. Another is the plasmonic coupling between the approaching AgNPs after the volume phase transition.As shown in Fig.2 (d), the distances between the AgNPs inside the collapsed AgNPs/(PNIPAM/PAA IPN) hybrid microgels are mostly less than 10 nm, at which the neighboring AgNPs have strong plasmonic coupling effect.[21] For the same hybrid microgels, the pH induced change of the AgNPs' LSPR wavelengths at 40℃is more noticeable than that at 20℃. This behavior is presumably because of the fact that the distances between the approaching AgNPs within the collapsed microgel networks at 40℃ above their volume phase transition temperature are further shortened after pH decrease triggered shrinking, leading to stronger plasmonic coupling effect. The appearance of AgNPs/(PNIPAM/PAA IPN) hybrid microgels (IPN-Ag-1) dispersion at pH=3.0 or 7.0 is shown in Fig.S3 in the Supporting Information. It exhibits semi-transparent orange-red liquid at pH=3.0, whereas showing transparent orange-yellow liquid at pH=7.0. From this phenomenon it can be expected that the hybrid microgels are used as colormetric devices for measuring pH value. Fig. S4 (a) and (b) illustrate the UV-vis spectra of the hybrid microgels IPN-Ag-3 dispersion with alternating pH values between 4.0 and 5.0 at the temperature of 20℃ or 40℃, respectively. It can be found that at the two temperatures its UV-vis spectroscopy change with alternating pH is reversible, exhibiting that the plasmonic property of the AgNPs inside the hybrid microgels can be reversibly tuned by pH value.

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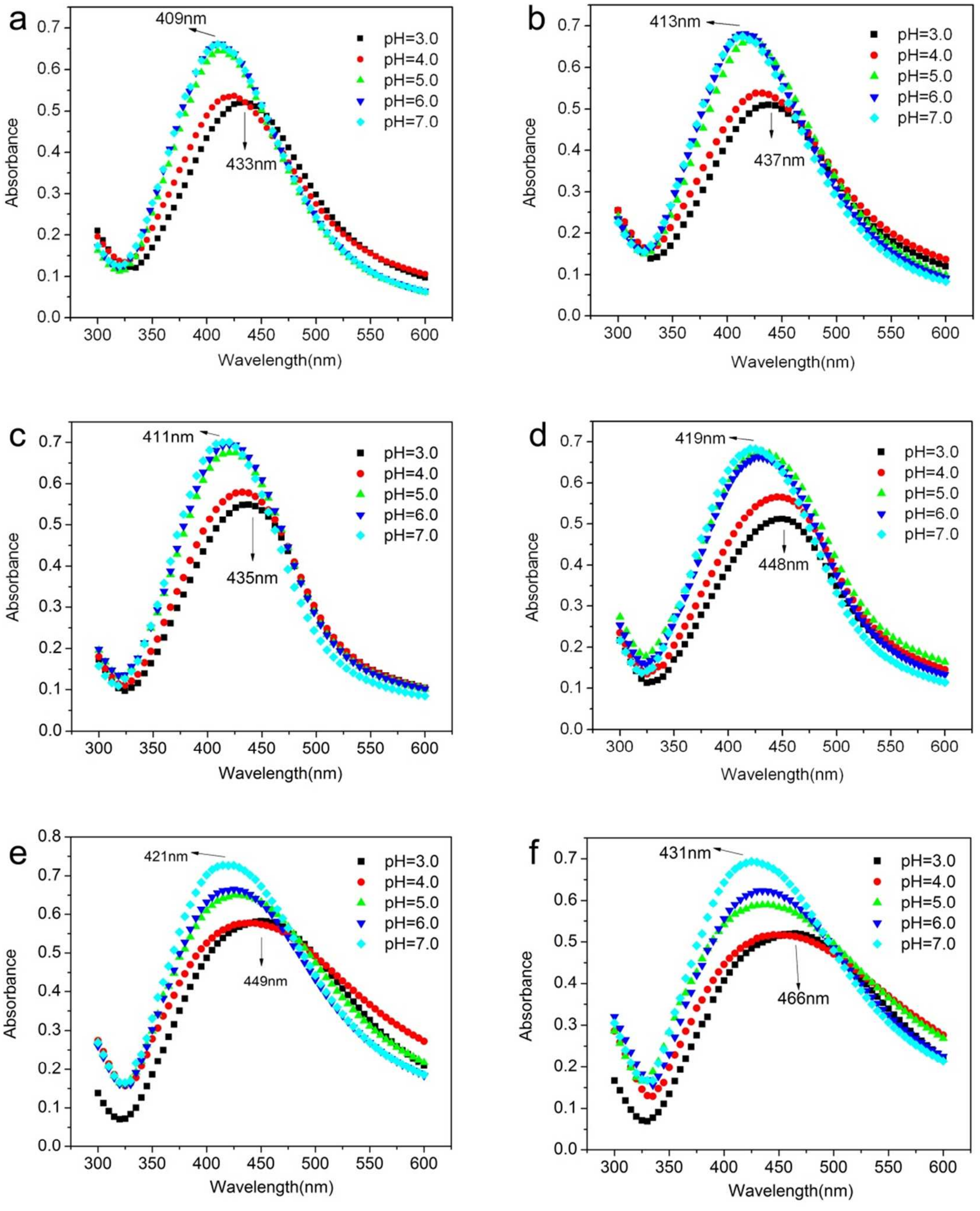

Fig.5 UV-vis spectra of AgNPs/(PNIPAM/PAA IPN) microgels with different AgNPs content at various pH values under the temperature of 20℃ or 40℃ (IPN-Ag-1: 20℃ (a), 40℃ (b); IPN-Ag-2:20℃ (c), 40℃ (d); IPN-Ag-3:20℃ (e), 40℃ (f)).

Therefore, it can be deduced that their temperature tunable plasmonic property is due to increase of the refractive index around the AgNPs inside the hybrid microgels resulting from expelling of a large amount of water upon temperature triggering volume phase transition. In addition, during the transition of the hybrid microgels, the embodied AgNPs approach with each other, leading to their plasmonic coupling. This may also result in the temperature tunable plasmonic property of the AgNPs inside the microgels. Regardless of pH condition, within the same temperature range, their LSPR wavelength change magnitude with temperature is increased with their content inside the hybrid microgels, indicating that the tunability of their plasmonic property by temperature is enhanced with their content. This phenomenon is also due to the fact that the distances between the entrapped AgNPs inside the hybrid microgels become shorter with increasing their content, resulting in stronger plasmonic coupling effect induced by temperature change. For the same hybrid microgels, within the temperature range from 20℃ to 40℃, the LSPR wavelength change magnitude at pH 3.0 is larger than that at pH 7.0. At pH 3.0, the PAA network within the microgels is collapsed, and the AgNPs approach with each other. If temperature triggering volume phase transition makes them further approach, their plasmonic coupling is highly enhanced, leading to more noticeable redshifting of their LSPR wavelength. Fig.S6 (a) and (b) are the UV-vis spectra of the hybrid microgels (IPN-Ag-3) at alternating temperatures between 20 ℃ and 40℃ under pH =3.0 or 7.0, respectively. It can be found that, under the two pH values, their UV-vis spectroscopy change with alternating temperatures is reversible, exhibiting that the plasmonic property of the AgNPs within the hybrid microgels can be reversibly tuned by temperature.

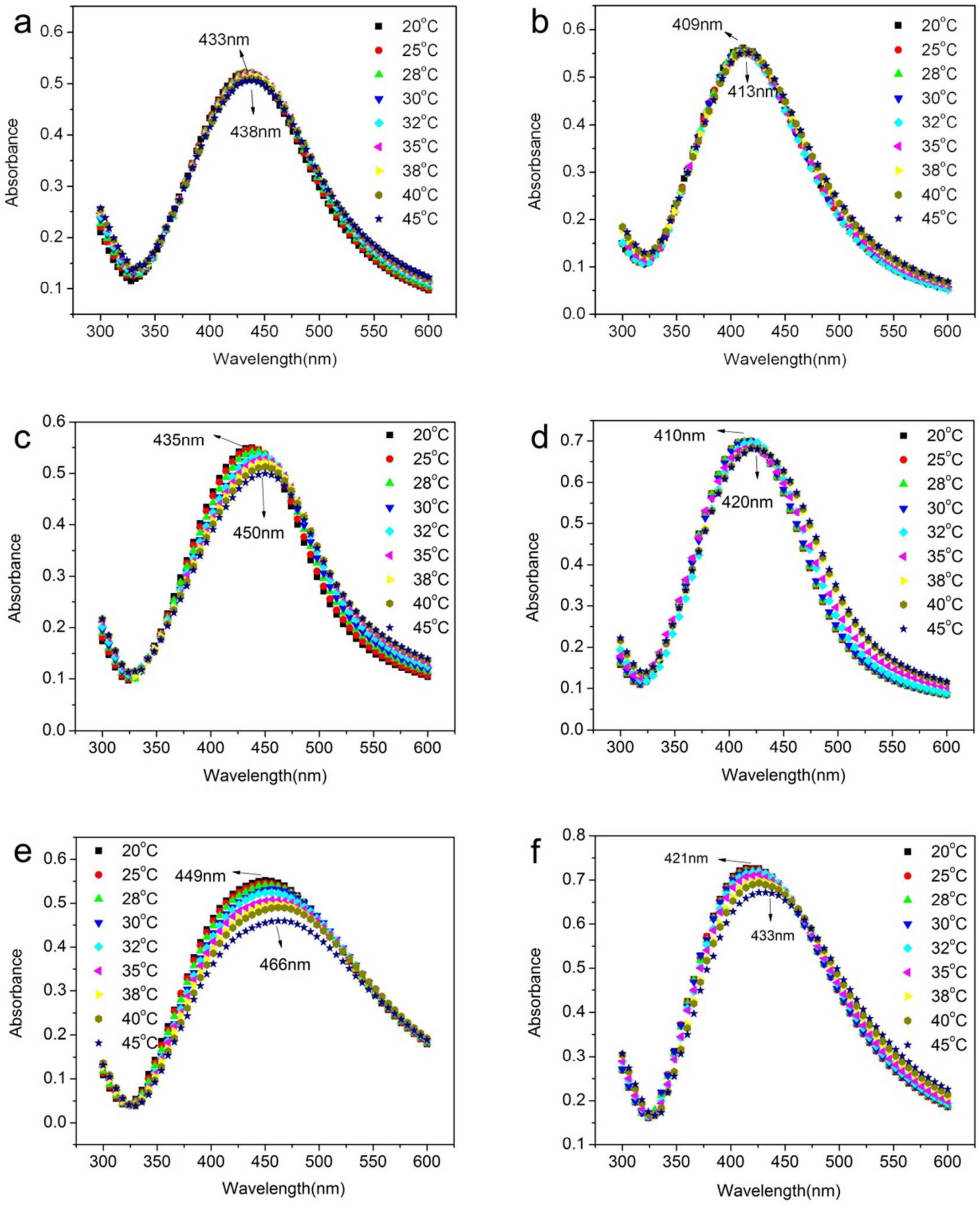

Fig. 6 UV-vis spectra of AgNPs/(PNIPAM/PAA IPN) microgels with different AgNPs content at various temperature under pH=3.0 or 7.0 (IPN-Ag-1:pH=3.0(a)， pH=7.0(b); IPN-Ag-2: pH=3.0(c), pH=7.0(d); IPN-Ag-3: pH=3.0(e), pH=7.0(f)).

pH and temperaturetunable SERS efficiency of AgNPs/(PNIPAM/PAA IPN) hybrid microgels

Using the AgNPs/(PNIPAM/PAA IPN) hybrid microgels(IPN-Ag-3) as substrates, the SERS spectra of PMBA as probing molecules with a concentration of 10^{-6} M in aqueous solutionat20℃ or 40℃were measured at different pH values, as shown in Fig.7 (a) and (b), respectively. According to the previously reported SERS spectra of PMBA on Ag and Au substrates,[22] the two prominent peaks at 1076 and 1587 cm^{-1} are assigned to its aromatic ring breathing vibration. Additional two marked peaks with lower intensity at 1183 and 1368 cm^{-1} (pH=7.0) are attributed to CH bending vibration and $-COO^{-}$ stretching vibration, respectively. The SH stretching vibration peak at ca. 2580 cm^{-1} present in the Raman spectrum of PMBA powder is absent in the SERS spectra, as shown in Fig.S7 (a) and (b), indicating that PMBA is bound to the AgNPs entrapped within the microgels through its mercapto group. Comparing Fig.S7 (b) and (c), it can be concluded that no Raman signal of PNIPAM and PAA polymers within the SERS substrate appears in the spectra of Fig.7. As seen from Fig.7, whether at 20℃ or 40℃, all peaks other than the one at 1368 cm^{-1} are strongly enhanced with decreasing pH values from 7.0 to 3.0. The area of 1587 cm^{-1} peak as a function of pH at 20℃ or 40℃ is depicted in Fig. S8 (a) and (b), respectively. At both temperatures, its drastic change occurs within the pH range from 4.0 to 6.0, in agreement with the one for the particle size and LSPR wavelength change of AgNPs/(PNIPAM/PAA IPN) hybrid microgels with pH. Therefore, it could be speculated that the pH induced SERS signal enhancement of PMBA is associated with pH triggered volume phase transition of the hybrid microgels as SERS substrates. As discussed above, the plasmonic coupling between the closely approached AgNPs inside the collapsed microgels is present, which would lead to drastic electric field (E) enhancement within their gaps according to the estimation by Yin and Fang et al.[17, 23] In light of electromagnetic enhancement mechanism, the enhancement factor (EF) of SERS is about proportional to E^4, so the maximum EF could reach a magnitude of 10^8. Although only few PMBA molecules are located within the gaps, their contribution to whole EF should be pronounced due to the huge enhancement effect. It can be affirmative that the molecules located within the gaps become more and more with pH change driving the microgels shrinking. Thus, it is not difficult to understand that the most prominent

SERS signal change occurs during pH induced volume phase transition of the hybrid microgels. According to electromagnetic enhancement mechanism, all peaks of the probing molecules in their SERS spectrum should be equally enhanced by plasmonic coupling, without selectivity. Then, why is only the peak at 1368 cm^{-1} in Fig.7 neither strongly enhanced with pH lowering like other peaks, nor weakened like that using bare Ag nanoparticles as substrates, as reported previously.[24] This is probably due to the counterbalance of two effects, i.e. electric field enhancement coming from the plasmonic coupling between the AgNPs and decrease of the -COO^{-} groups owing to their protonation with pH lowering. Comparing Fig. S8 (a) and (b), it can be found that, within the same pH range, the change of 1587 cm^{-1} peak area at 40℃ is more noticeable than that at 20℃. This phenomenon is equally due to the fact that the distances between the approached AgNPs within the collapsed PNIPAM/PAA IPN microgels at 40℃ above their volume phase transition temperature are further shortened after subsequent pH decrease triggered volume phase transition, leading to stronger plasmonic coupling and electric fields within their gaps. Because of reversibility of the plasmonic coupling effect between the AgNPs inside the hybrid microgels, it can be assumed that their SERS efficiency associated with the effect should be tuned reversibly by pH. The assumption was proved by measuring the SERS spectrum of PMBA using the AgNPs/(PNIPAM/PAA IPN) hybrid microgels (IPN-Ag-3) as substrates alternately between pH 4.0 and 6.0. As shown in Fig. S9 (a) and (b), whether at 20℃ or 40℃, its 1587 cm^{-1} peak area is by and large reversible with the pH cycling.

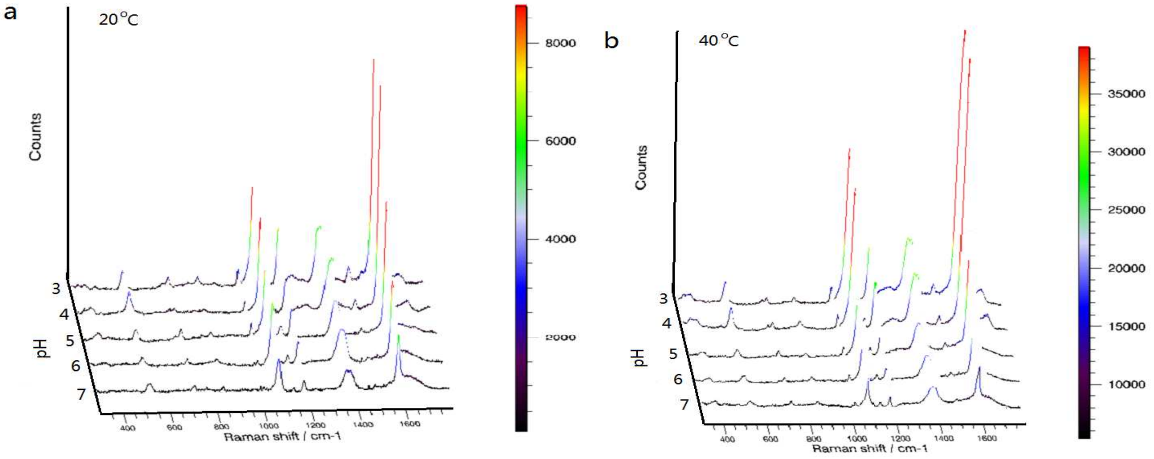

Fig.7 SERS spectra of 10^{-6} M PMBA aqueous solution using AgNPs/(PNIPAM/PAA IPN) hybrid microgels (IPN-Ag-3) as substrates at different pH values under 20°C (a) or 40°C (b).

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The effect of temperature on the SERS efficiency of AgNPs/(PNIPAM/PAA IPN) hybrid microgels as substrates was investigated using PMBA as probing molecule under pH 4.0 or 6.0, as illustrated in Fig. 8 (a) and (b), respectively. Under both pH conditions, all peaks in its SERS spectrum are remarkably enhanced as temperature is raised from 20℃ to 45℃. The plot of the area of 1587 cm^{-1} peak as a function of temperature under pH=4.0 or 6.0 is exhibited in Fig. S10 (a) and (b), respectively. Under both pH conditions, its marked change occurs within the temperature range from 25℃ to 40℃, also in agreement with the one for the particle size and LSPR wavelength change of AgNPs/(PNIPAM/PAA IPN) hybrid microgels with temperature. Similar to above mentioned pH effect on the SERS strength of PMBA, the temperature elevation driven SERS signal enhancement also results from the plasmonic coupling between the approached AgNPs within the hybrid microgels after the temperature triggered collapse of their PNIPAM networks. Under pH 4.0 or 6.0, the SERS spectra of 10^{-6} M PMBA in aqueous solution were measured using IPN-Ag-3 microgels as substrates by changing temperature between 20℃and 40℃ alternately. As shown in Fig. S11 (a) and (b), whether under pH 4.0 or 6.0, their 1587 cm^{-1} peak areas are basically reversible with the temperature cycling, indicating that the SERS efficiency of AgNPs/(PNIPAM/PAA IPN) hybrid microgels can be tuned reversibly by temperature. In addition, it can be concluded from Fig.7 and Fig.8 that the SERS intensity of PMBA with the same concentration under 40℃ and pH=4.0 is more than 10 times stronger than that under 20℃ and pH=6.0. This result indicates that pH and temperature change stimuli can be simultaneously used to enhance SERS intensity when employing AgNPs/(PNIPAM/PAA IPN) hybrid microgels as SERS substrates.

In order to evaluate the feasibility of using AgNPs/(PNIPAM/PAA IPN) hybrid microgels as SERS microsensors for probing temperature and pH value, the SERS spectra of 10^{-6} M PMBA in aqueous solution as molecular probe were measured five times at two temperatures under pH=6.0 or under two pH values at 25℃, respectively. Based on the curve in Fig.S10 (a) as calibration curve, the temperatures were obtained from 1584 cm^{-1} peak areas on the measured SERS spectra, as listed in Table S1. The two average temperatures are 24.3℃ and 38.5℃, respectively, very close to their actual values (24.0℃ and 38.0℃). Their relative standard deviations (RSDs) are 9.6% and 5.7%, indicating that the result measured at higher temperature maybe has better reproducibility. As listed in Table S2, the pH values were also obtained from 1584 cm^{-1} peak areas on the measured SERS spectra based on the curve in Fig.S8 (a) as calibration curve. The two average pH values are 3.8 and 6.2, respectively, also approaching their actual values (4.0 and 6.0). Their RSDs are 7.9 and 3.2, respectively, lower than those for measuring temperature. This could reveal that the reproducibility for measuring pH value using AgNPs/(PNIPAM/PAA IPN) hybrid microgels as SERS microsensors is higher than that for measuring temperature, especially for measuring higher pH value.

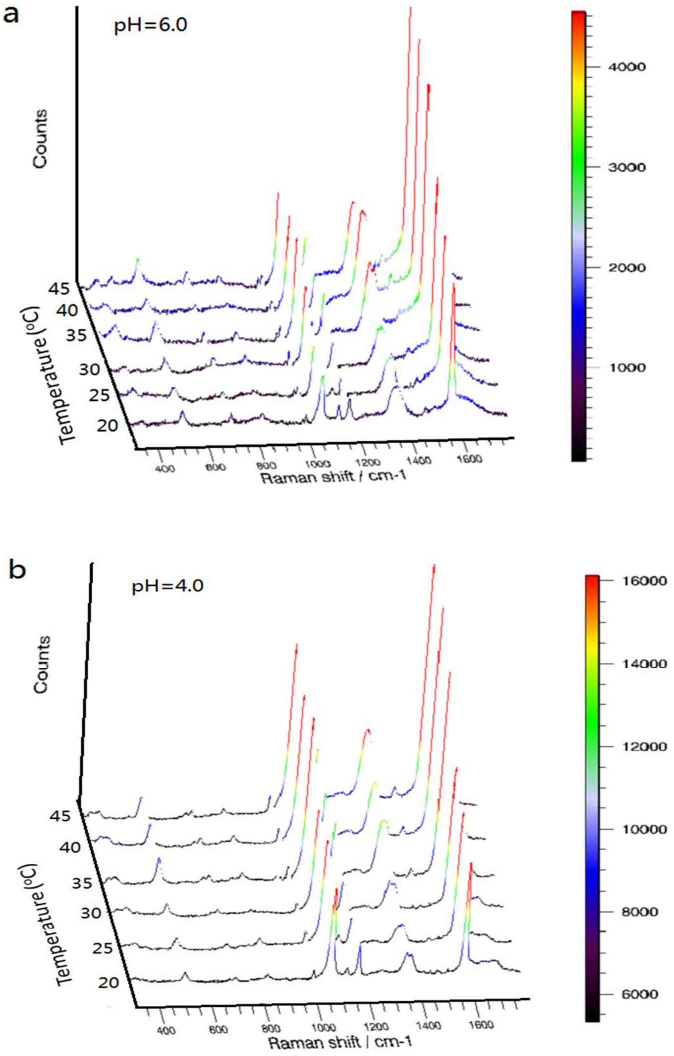

Fig.8 SERS spectra of 10^{-6} M PMBA aqueous solution using AgNPs/(PNIPAM/PAA IPN) hybrid microgels as substrates at different temperatures under pH 6.0 (a) or pH 4.0 (b)

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Conclusions

The pH/temperature dual stimuli responsive hybrid microgels with little interference between two stimulus-responsive components were prepared by loading AgNPs into the microgels with IPN structure composed of separately crosslinked PAA and PNIPAM by in-situ reduction of Ag^+ ions. AgNPs are homogeneously distributed within the microgels, and their particle diameters are within the range of 11 to 15 nm and their weight content can top 38%. The LSPR wavelength of the AgNPs inside the hybrid microgels can be reversibly tuned by temperature within the range from 20℃to 45℃or pH value from 3.0 to 7.0, and the tunability is enhanced by their content. When the hybrid microgels were used as SERS substrates for detecting 10^{-6} M PMBA in aqueous solution, its SERS intensity is remarkably increased as the pH value of the hybrid microgels dispersion is reduced from 7.0 to 3.0. Additionally, as the measuring temperature is raised from 20℃to 45℃, its SERS signal is also noticeably strengthened. If the two stimuli are simultaneously exerted, the SERS intensity is greatly elevated. The hybrid microgels can be used as SERS microsensors for measuring both pH value and temperature.

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Notes and references

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Table of contents entry

Plasmonic property and SERS efficiency of the silver nanoparticles embeded within the microgels with interpenetrating polymer network structure can be reversibly tuned by temperature and pH value