Monodisperse Thermo-responsive Composite Microgels with Core-shell Structure based on Au@Ag Bimetallic Nanorod as Core: Fabrication and Application in SERS Substrate

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ABSTRACT

The monodisperse Au@Ag bimetallic nanorod is encapsulated by crosslinked poly(N-isopropylacrylamide) (PNIPAM) to produce thermo-responsive composite microgel with well-defined core-shell structure (Au@AgNR@PNIPAM microgel) by seed-precipitation polymerization method using butenoic acid modified Au@AgNRs as seeds. Their core-shell structure and thermo-responsive property were identified using electron transmission microscopy (TEM) and dynamic light scattering technique (DLLS), respectively. As the temperature is raised from 20 to 50℃, their particle size decreases sharply, particularly within the temperature range of 30 to 40℃.The longitudinal localized surface plasmon resonance wavelength of the composite microgels measured by ultraviolet visible (UV-vis) spectroscopy is red-shifted from 677 to 704 nm within the same temperature range, indicating that their plasmonic property is temperature-tunable. When the composite microgels are used as SERS substrates for detection of 2×10^{-5} M 1-naphthol in aqueous solution, its SERS signal strength is greatly enhanced as the temperature is elevated from 25 to 45℃, maybe due to existence of the entrappment effect for the analyte during their temperature triggered volume phase transition.

Keywords: smart composite microgels, core-shell structure, Au@Ag bimetallic nanorods, thermo-responsiveness, surface enhanced Raman spectroscopy

1 INTRODUCTION

Surface enhanced Raman spectroscopy (SERS) is a powerful analytical technique that allows ultra-sensitive chemical or biochemical analysis [1]. However, so far this technique is not widely used in analysis and detection due to the following two limitations. One is low reproducibility of the SERS signal due to structure and composition inhomogeneity of the SERS substrate across its surface or from batch to batch, which is detrimental to quantitative analysis [2]. Another is that 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 [3]. 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 [4]. Therefore, to improve SERS signal reproducibility and widen its application scope are the future two significant research subjects of SERS technique.

The noble metal nanoparticles like Au or Ag nanoparticles are among the most commonly used SERS substrates, because of their simple and cost-efficient bottom-up production, e.g., by adding reducing agents to aqueous solution of the metallic salts. It is well known that rod-shaped noble metal nanoparticles have highly stronger SERS activity than the corresponding spherical ones owing to the so called “lightning-rod effect” [5]. The performance of Ag nanorods in enhancing Raman signals has been found to be much better than that of the AuNRs of the same size [6]. This is because Ag nanorods exhibit much stronger surface electric field under plasmonic resonant excitation condition than the corresponding AuNRs [7]. Although core-shell structured bimetallic nanorods based on AuNR as core and Ag as shell (Au@AgNRs) have been extensively studied by many groups since 2001 [7], [8], [9], to our best knowledge, the Au@AgNRs with narrow size and shape distribution have not been reported so far.

Monodisperse Au@Ag bimetallic nanorods are expected to have fascinating application perspective in surface enhanced Raman scattering (SERS) technique, since they have the following advantages: (1) high reproducibility of SERS signal due to their size and shape monodispersity; (2) high sensitivity resulting from their rod-like shape and Ag surface; (3) high chemical stabiltiy owing to free electron transfer of Au core to Ag shell. Even so, they are not able to be used as SERS substrate for detecting the analyte having low affinity towards metal surface, such as 1-naphthol. To address the probem, here monodisperse Au@Ag bimetallic nanorod is encapsulated by crosslinked poly(N-isopropylacrylamide) (PNIPAM) to produce thermo-responsive composite microgel with well-defined core-shell structure (Au@AgNR@PNIPAM microgel) by seed-precipitation polymerization method using butenoic acid modified Au@AgNRs as seeds.

2 EXPERIMENTAL

2.1 Materials

N-isopropylacrylamide (NIPAM) (purity 95%, TCI) was purified by repeated recrystallization from n-hexane/benzene (v/v:40/60) mixed solvent. N, N'-methylene bisacrylamide (MBA) (purity 95%, Aldrich), 2, 2'-azobis(2-amidinopropane hydrochloride) (AAPH) (purity 98%, Aldrich), butenoic acid (BA) (purity 96%, Aldrich) and 1-napthol (purity 99%, Aldrich) were used as purchased. All deionized water used in the synthesis and characterization was made using a Millipore Direct-Q system.

2.2 Preparation of Au@AgNR@PNIPAM Microgels

Monodisperse AuNRs with diameter 20 nm and aspect ratio 3.1 were synthesized by binary surfactant method reported by Ye et al. [10]. Then, the AuNRs were used as seeds for the synthesis of monodisperse Au@AgNRs. Briefly, to glycine buffer solution at pH = 8.9 (adjusted with 1.0 M NaOH solution), the AuNRs solution and $AgNO_3$ aqueous solution were added. Subsequently, ascorbic acid aqueous solution was added under gentle magnetic stirring. After 12 h, the solution was purified by centrifugation. Then, BA was added to the purified Au@AgNRs aqueous dispersion at 70℃. After 1 h, the dispersion was centrifuged to remove excessive BA. The BA modified Au@AgNRs dispersion was heated to 70℃ under N_2 flow and NIPAM and MBA was added under magnetic stirring. After 15 min, the polymerization was initiated with addition of AAPH. After 30 min, the obtained dispersion was allowed to cool down to room temperature. The dispersion was purified, and the precipitated composite microgels were redispersed in equivalent volume of deionized water.

2.3 Characterization and Measurement

The morphological structure of Au@AgNR@PNIPAM composite microgels was characterized using TEM (2100F, JOEL) at a voltage of 200 kV. The average hydrodynamic diameters (D_H) of the microgels dispersed in water at different temperatures were measured via DLLS (BI-200SM, Brookheaven). The localized surface plasmon resonance (LSPR) wavelengths of the Au@AgNR inside composite microgels at varied temperatures were determined from their UV-Vis-NIR adsorption spectra (Lambda 35, Perkin-Elmer). SERS spectra at different temperatures were measured on a micro-Raman system (inVia-Reflex, Renishaw) equipped with a multi-channel charge-coupled device detector and a confocal microscope (DM2500 M, Leica) upon excitation by 633 nm laser line.

3 RESULTS AND DISCUSSION

The typical TEM picture of Au@AgNR@PNIPAM composite microgels is shown in Figure 1, which exhibits that the composite microgels have well-defined core-shell structure with a centered single Au@AgNR and good monodispersity (their particle size's polydispersity index determined by DLLS is 0.07), and no pure PNIPAM microgels were found.

Due to thermo-responsive property of the PNIPAM shells, the hydrodynamic diameter (D_H) of Au@AgNR@PNIPAM microgels determined by DLLS is a function of temperature, as illustrated in Figure 2. As the temperature of their aqueous medium is raised from 20℃ to 50℃, their D_H decreases from 303 nm to 198 nm. Their volume phase transition temperature (VPTT), at which their volume is the most sharply varied, is about 35℃, slightly higher than the one of pure PNIPAM microgels (about 33℃), possibly due to the restraining effect of the embodied Au@AgNR on the PNIPAM shell within the composite microgels.

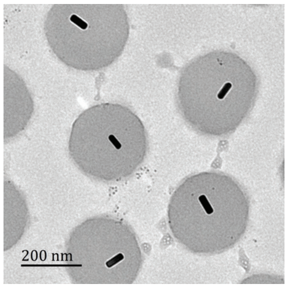

Figure 1: TEM image of Au@AgNR@PNIPAM microgels

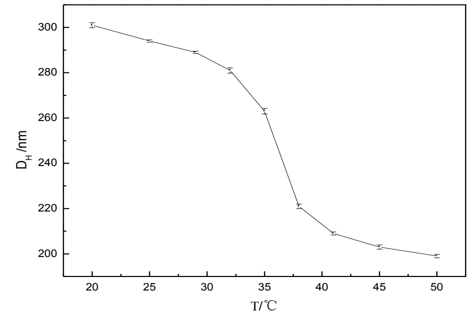

Figure 2: Hydrodynamic diameters (D_H) of Au@AgNR@PNIPAM microgels at different temperatures

Figure 3 illustrates UV-vis-NIR spectra of Au@AgNR@PNIPAM composite microgels in diluted aqueous dispersions at various temperatures. The two extinction peaks at 500 nm and 700 nm are attributed to the transverse and longitudinal LSPR wavelength of the AuNRs entrapped within the microgels, respectively. Another peak at 400 nm should be attributed to an octupolar plasmon mode of Au@AgNRs. As the temperature is raised from 20℃ to 50℃, their transverse LSPR wavelengths are little shifted, but their longitudinal ones are increased from 677 nm to 704 nm. Since no plasmonic coupling is present between the entrapped Au@AgNRs due to the physical barriers imposed by their PNIPAM shells, the longitudinal LPSR wavelength red-shift of Au@AgNR@PNIPAM microgels with temperature raising is only attributed to the local refractive index increase around the Au@AgNR resulting from water expelling during their temperature induced volume phase transition.

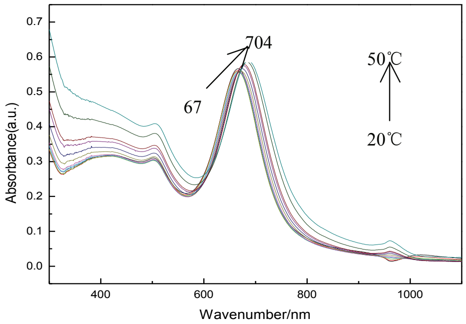

Figure 3: UV-vis spectra of Au@AgNR@PNIPAM microgels in diluted aqueous dispersion at various temperatures

The SERS activity of Au@AgNR@PNIPAM composite microgels at different temperatures was evaluated by recording spectra of 1-napthol (1NOH), which is a relevant biomarker for quantifying the exposure to polycyclic aromatic hydrocarbons in urine, as well as the presence of carbaryl pesticides in the environment or in fruits [11]. The SERS spectra of 1NOH in 2×10^{-5}M aqueous solution using the composite microgels as substrate upon excitation with 633 nm laser line at various temperatures are exhibited in Figure 4. They are identically characterized by aromatic ring breathing (1577cm^{-1}, 1390cm^{-1}), C-H bending (1447 cm^{-1}) and C-O stretching (1280 cm^{-1}). As illustrated in Figure 4, the SERS intensity of 1NOH at the temperature above the VPTT of Au@AgNR@PNIPAM microgels is about 4 times higher than that below their VPTT. Due to absence of plasmonic coupling between the enbodied Au@AgNRs, which is able to lead to enhancement of the SERS signal of the analyte absorbed on the metal nanoparticles as reported by our group [12], here the SERS signal enhancement may only originate from the entrapment effect of the thermo-responsive substrate for 1NOH. As discussed by Alvarez-Puebla et al. [13], the temperature triggered volume phase transition of the substrate can trap hydrophobic 1NOH molecules and get them sufficiently close to the Au@AgNR core for providing the SERS signal. When the temperature is elevated from 25℃ to 45℃, as mentioned above, Au@AgNR@PNIPAM composite microgels are gradually shrunk and their PNIPAM chains become more and more hydrophobic, so increasing 1NOH molecules with relatively strong hydrophobicity are trapped into their interiors and approached toward the metal surfaces, resulting in gradually enhancing SERS signal. The temperature range for rapid SERS signal increase is the same as the one for its volume or longitudinal LSPR wavelength change with temperature.

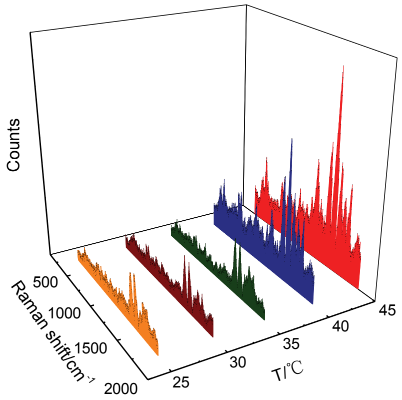

Figure 4: SERS spectra of 2×10^{-5} M 1-naphthol in aqueous solution using Au@AgNR@PNIPAM microgels as SERS substrate in the heating process from 25°C to 45°C

4 CONCLUSIONS

In summary, monodisperse Au@Ag bimetallic nanorod is encapsulated by crosslinked poly(N-isopropylacrylamide) (PNIPAM) to produce thermo-responsive composite microgel with well-defined core-shell structure (Au@AgNR@PNIPAM microgel) by seed-precipitation polymerization method using butenoic acid modified Au@AgNRs as seeds. Their core-shell structure and thermo-responsive property were identified using TEM and DLLS respectively. The UV-vis spectroscopy results indicate that the composite microgels have unique plasmonic property, and their longitudinal wavelength can be readily tuned by temperature. When the composite microgels are used as SERS substrates, the activity is remarkably increased with their temperature triggered volume phase transition.

5 ACKNOWLEDGEMENT

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