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Designing and fabricating composites of PNIPAM@Au nanorods with tunable plasmon coupling for highly sensitive SERS detection

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ABSTRACT

In this study, hybrid substrates composed of poly(*N*-isopropylacrylamide) hydrogels and Au nanorods (PNIPAM@AuNRs) that exhibit tunable plasmon coupling are designed and fabricated. In this process, Au NRs are deposited on the surface of a PNIPAM hydrogel, and the temperature is increased, causing the hydrogel template to shrink, thereby driving the Au NRs closer to each other. The resulting surface plasmon resonances (SPR) of the composite are observed as a large red-shift. The formation of more hot spots increases the already high sensitivity of surface-enhanced Raman scattering (SERS) detection, and the tunable optical properties enable closer matching of the laser to the near-infrared excitation required. Moreover, these hybrid substrates can be conveniently identified by optical microscopy, enabling in situ SERS detection with high sensitivity and reproducibility.

1. Introduction

Because of their enhanced particle polarizabilities, Au nanorods (NRs) are ideal candidates for applications involving manipulations of incident light and sensitive molecular spectroscopy. Au nanorods have two distinct length scales and exhibit two surface plasmon resonances (SPRs). The longitudinal SPR (LSPR) is observed at wavelengths ranging from the visible region to the near-infrared (NIR) region, greatly increasing their range of applications [1–5]. The lasers of portable Raman equipment usually operate at approximately 785 nm, which is better matched by substrates composed of Au NRs than by substrates composed of Au nanospheres. In addition, Au NRs are attractive for biomedical applications because the human body is transparent to light in the 600–900 nm region, a region referred to as the “NIR window” [6–8].

The aspect ratios (ARs) of anisotropic NRs have been observed to play a role in the LSPR region, so the most versatile approach to adjusting the LSPR is to control the AR of the associated Au NRs [9,10]. In this case, the LSPR will shift to longer wavelengths when the AR of the NRs increases. Recent advances in synthetic techniques have yielded a wide range of Au NRs exhibiting different ARs. Assembling Au NRs into chains also results in a red or blue shift of the longitudinal LSPR [11,12]. Thus, many approaches involve changing the arrangements of Au NRs; one such example consists of plasmonic structures constructed from Au NRs combined with molecular linkers or templates. In particular, small sulfydryl-containing molecules and DNA are often used to link NRs. Jana et al. have fabricated high-quality, specifically sized Au-NR samples with different ARs using the self-assembly of surfactant-assisted NRs [13]. Lee and co-workers have taken advantage of the geometrical and chemical anisotropies of NRs to form corresponding ordered assemblies into chains and have established a direct correlation between ensemble-averaged surface-enhanced Raman scattering (SERS) and the extinction properties of these chains [14]. However, regardless of whether different Au NRs with specific ARs are fabricated via direct synthesis or via linking, the flexibilities of the resulting plasmonic nanostructures are reduced. Their LSPRs are fixed, disabling the ability to match the laser excitation wavelength and decreasing sensitivity. It is thus desirable to synthesize suitable plasmonic structures in which the coupling of Au NRs can be switched flexibly.

Conversely, thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) microgels have been widely used as templates for immobilizing Au or Ag nanoparticles, most importantly because this procedure enables fine-tuning of the distance between metal nanoparticles, determined when a microgel template undergoes a phase transition, by simply changing the temperature [15,16]. Shrinkage of the microgel not only pushes the metal nanoparticles together, generating highly active hot spots, but also causes the SPR of the composite to undergo an obvious red shift [17–19]. In previous studies, our groups have developed SERS substrates

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composed of PNIPAM templates and Ag nanoparticle composites in which the gap between Ag nanoparticles can be modulated from 30.4 nm to 4 nm, thereby increasing SERS intensities by three orders of magnitude [20,21]. The tunability enabled by plasmon coupling in these SERS-active nanostructures causes their SPRs to exhibit red or blue shifts, thereby enabling more flexibility in applications employing plasmonic sensing.

Herein, we report a new composite SERS substrate composed of a PNIPAM template in which the LSPRs of Au NRs can be induced to undergo red shifts as a result of increasing temperatures. The advantages of this new composite are threefold. First, the formation of more hot spots, which accompanies the shrinking of the thermo-sensitive template, increases the sensitivity of SERS detection. Second, the tunable optical properties of the composite facilitate closer matching to the near-infrared excitation laser. Finally, it is hoped that this substrate can be employed in a portal Raman instrument with a laser wavelength of 785 nm and that this instrument can be applied to detection within the human body.

2. Experimental

2.1. Reagents

All chemicals were analytical reagent grade and were used as received. Cetyltrimethylammonium bromide (CTAB), chloroauric acid tetrahydrate ($HAuCl_4 \cdot 3H_2O$), trisodium citrate dehydrate (NaCt), silver nitrate ($AgNO_3$), nitric acid (HNO_3), sodium borohydride ($NaBH_4$), ascorbic acid (AA), N-isopropylacrylamide (NIPAM, 97%), glycine (98.5%), *N*,*N*′-methylene bisacrylamide (BIS), thiram, crystal violet (CV), and potassium persulfate (KPS) were purchased from Shanghai Chemical Reagent Ltd. Co. of China. All solutions were prepared using ultrapure water (resistance >18 $M\Omega\,cm^{-1}$).

2.2. Apparatus

Scanning electron microscopy (SEM) images were obtained using a Sirion 200 field emission scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 instrument operated at 100 kV. Ultraviolet–visible (UV–vis) absorption spectra were collected on a Solidspec-3700 spectrophotometer. Raman spectra were generated using a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon). Using a 50× microscope objective, the laser beam was focused on a sample that was approximately 1 μm in size. The laser power was approximately 1 mW, and the recording time was 1 s for each spectrum.

2.3. Sample preparation

2.3.1. PNIPAM template with negative charge

The temperature of a 20-mL aliquot of ultrapure water was raised to 70 °C. The water was purged with nitrogen for 15 min, after which NIPAM (0.2260 g) and BIS (0.0160 g) were added. After stirring for 15 min, polymerization was initiated by the dropwise addition of KPS (0.0200 g of KPS powder dispersed in 1 mL of water). After 5–10 min, the colourless solution became turbid, and the reaction was allowed to proceed for 2 h at 70 °C. The white mixture was then allowed to cool to room temperature under stirring. To remove small oligomers and unreacted monomers, the dispersion was centrifuged (40 min at 6000 rpm), and the precipitate was washed three times with ultrapure water and then re-dispersed in 15 mL of water.

2.3.2. Au NRs with different ARs

Au NRs composed of two different types of ARs were prepared using the typical seeds-growth method described elsewhere

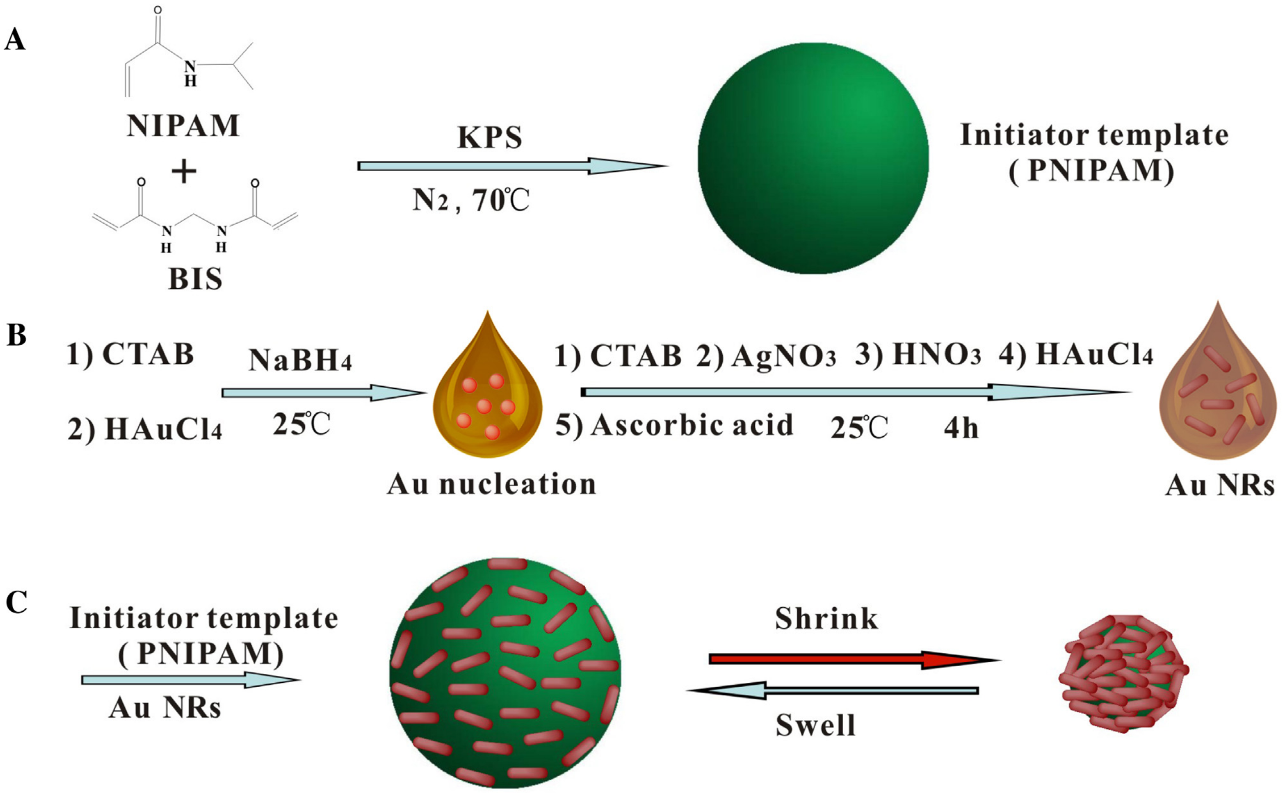

Fig. 1. Schematic of the synthesis process for PNIPAM/AuNRs composites.