Amplifying the signal of localized surface plasmon resonance sensing for the sensitive detection of Escherichia coli O157:H7

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Gold nanorods (Au NRs) based localized surface plasmon resonance (LSPR) sensors have been widely employed in various fields including biology, environment and food safety detection, but their size- and shape-dependent sensitivity limits their practical applications in sensing and biological detection. In our present work, we proposed an approach to maximally amplify the signal of Au NRs based LSPR sensing by coating an optimized thickness of mesoporous silica onto Au NRs. The plasmonic peaks of Au NRs@SiO₂ with different shell thickness showed finely linear response to the change of surrounding refractive index. The optimized thickness of mesoporous silica of Au NRs@SiO₂ not only provided high stability for LSPR sensor, but also displayed much higher sensitivity (390 nm/RIU) than values of Au NRs from previous reports. The obtained Au NRs@SiO₂ based LSPR sensor was further used in practical application for selectively detection of the E. coli O157:H7, and the detection limit achieved 10 CFU, which is much lower than conventional methods such as electrochemical methods and lateral-flow immunochromatography.

The localized surface plasmon resonance (LSPR) is a spectroscopic phenomenon based on the resonant oscillations of free electrons of various materials including noble metal nanoparticles, Al nanoparticles, conventional semiconductors and 2D materials, when stimulated by incident light⁴⁻⁶. Except the size, shape⁴⁻⁶ and composition of nanoparticles, the frequency and intensity of the LSPR bands are sensitive to the interparticle spacing and dielectric environment⁶⁻⁷. Therefore, the response of plasmonic nanoparticles to the refractive index variation of surrounding medium is employed to develop LSPR sensors in broad fields of biology, food, and environment⁸⁻¹¹. However, due to the low detection sensitivity and capacity⁷,¹²,¹³ and poor stability, the development of LSPR sensors is limited, especially in practical applications. For example, numerous efforts have been devoted to develop various methods for the detection of E. coli O157:H7, which is a gram-negative enteric bacteria, causing severe intestinal infections in humans¹⁴,¹⁵. Traditional methods ¹⁶⁻¹⁸ such as electrochemical methods and lateral-flow immunochromatography for detecting E. coli O157:H7 are always time-consuming and the sensitivity is not very high¹⁹⁻²¹ and limits their practical use as a commercial product. The objective of the present study is to develop a high performance LSPR sensor for practical application in real sample analysis (E. coli O157:H7) that would achieve high sensitivity and stability.

In recent years, some strategies were suggested to improve the sensitivity and stability of LSPR sensors such as morphology optimization of nanoparticles, surface functionalization and single nanoparticle detection²²,²³. Meanwhile, surface functionalization served as a powerful means not only to effectively improve sensitivity and stability of LSPR sensors but also flexibly modify plasmonic nanoparticles with desired functions for further applications²⁴. For example, polymer or biomolecules coated Au nanoparticles LSPR sensors show higher selectivity and stability²⁵.

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Homogeneous mesoporous silica has been proven to be a versatile biomaterial to directly improve stability of nanoparticles in complex bio-system, due to its excellent biocompatibility. On the other hand, mesoporous structure provides large-area and easy-decorated surface for maximally capturing the target molecules to improve the sensitivity of LSPR. Since the encapsulated SiO₂ determines the refractive index of surrounding environment, the thickness of SiO₂ attributed to a vital parameter to affect LSPR sensitivity. However, there is a controversial point about the effect of thickness of SiO₂ shell on LSPR sensitivity. For instance, Xu and co-workers synthesize 8 nm mesoporous silica shell coated Au NRs to improve the sensitivity to 325 nm/RIU. Wang and co-workers used 21 nm silica coated Au NRs to amplify the sensitivity for detecting biomolecules. Moreover, Huang and co-workers considered that a 2–3 nm silica shell coated on Au NRs induces a highest sensitivity for plasmonic organic photovoltaic devices. The recent theoretical calculation reveals that ultrathin silica coating (within 3.5 nm) would be ideal for improving the sensitivity. Therefore, the aim of our present work is to explore the cut-off thickness in a small size, and further amplify the sensitivity of Au NRs maximally for practical application for detection of E. coli O157:H7.

Herein, a series of Au nanorods (Au NRs) with different mesoporous silica shell are synthesized to study the effects of silica shell thickness on the sensitivity of Au NRs LSPR symmetrically. The as-prepared Au NRs@SiO₂ with optimal shell thickness showed high sensitivity and used as efficient LSPR biosensor to detect E. coli O157:H7. Au NRs with elongated geometry were selected as plasmonic nanoparticles for LSPR sensor due to their tunable and broad spectra range from the visible to near-infrared region. The thickness of SiO₂ on AuNRs was optimized by adjusting the concentration of Cetyltrimethyl Ammonium Bromide (CTAB) and the amount of tetraethyl orthosilicate (TEOS), achieving sensitive Au NRs@SiO₂. To verify the performance of Au NRs@SiO₂ as LSPR sensors, Au NRs@SiO₂ with optimal thickness was modified with specific antibody to selectively detect E. coli O157:H7 in high sensitivity. The detection limit of Au NRs@SiO₂ for E. coli O157:H7 is lower than 10 Colony-Forming Units (CFU), which is superior over the values of traditional methods.

Results and Discussion

Au NRs (Fig. 1 and 2A) were synthesized by using the seed-mediated growth method, which has an aspect ratio of 2.9. As prepared Au NRs showed typical horizontal and longitudinal LSPR bands at 530 nm and 726 nm, respectively (Fig. 2C). The number of Au NRs in solution was estimated to be 2.1 nM according to its extinction coefficient at the longitudinal plasmon peak (726 nm). According to the traditional method (soft-templating method), Au NRs were uniformly coated with mesoporous silica, forming nanorods@SiO₂ nanostructures (Fig. 1 and 2B). In the process of silica coating, CTAB formed a bilayer around Au NRs, which served as organic template for the formation of mesoporous silica shell. According to the general theory of statistics by measuring more than 100 particles, the thickness of other SiO₂ layers on Au NRs@SiO₂ (5, 10, 15, 20, 25 nm) were also confirmed by the general theory of statistics. CTAB was used as the template for depositing silica and many previous reports showed that lower concentration of CTAB resulting in thicker silica shell. Therefore, by adjusting the concentration of CTAB and the amount of TEOS, Au NRs@SiO₂ with different shell thickness could be prepared. The uniform silica shell endows a protective layer on the surface of Au NRs, leading to a lighter pink color (illustration of Fig. 2D).
to extremely stable Au NRs dispersion that could keep for three months at room temperature even after removal of CTAB.

Furthermore, the LSPR properties of Au NRs with different mesoporous silica shell were investigated by UV-vis absorption spectra (Fig. 4). The longitudinal plasmon bands of Au NRs@SiO$_2$ redshifted gradually with increasing the thickness of silica shell (Fig. 4A). The relationship between plasmon shift and thickness of silica is shown in Fig. 4B, indicating that the plasmon band shift showed approximately linearly with increasing shell thickness. This was ascribed to the refractive index variation of silica shell when changing the thickness. The refractive index of porous silica is much higher than the value of water. When the porous silica was coated onto the surfaces of Au NRs, the refractive index of surrounding environment of Au NRs increased, which was in accordance with previous work. Therefore, the coating of silica on Au NRs led to redshift of the longitudinal plasmon band, which proved that the Au NRs@SiO$_2$ was much sensitive to the change of surrounding refractive index than Au NRs. This allowed Au NRs@SiO$_2$ could be employed as a LSPR sensor based on the redshift of longitudinal plasmon band induced by coating with mesoporous silica.

To verify the performance of the Au NRs@SiO$_2$ based LSPR biosensor, Au NRs@SiO$_2$ was firstly used to test the surrounding refractive index variations, as shown in Fig. 5. The sensitivity was calculation according to the universal experienced formula:

$$\Delta \lambda = m \cdot \Delta n$$

(1)

$\Delta \lambda$ is the difference of the LSPR wavelength before and after coating; $m$ is the sensitivity; $\Delta n$ is the change in the refractive index.

The refractive index was tuned by adjusting the volume ratio of water and glycerol (from 0.9 to 0.1 with the volume ratio of 0.1 interval), and the refractive indices of the mixture solvents were calculated based on the Lorentz-Lorenz equation, as shown in the experimental details. Both of Au NRs and Au NRs@SiO$_2$ exhibited band redshift when increasing the volume ratio of glycerol to water (Fig. 5A and B).

The plasmon peaks of Au NRs and Au NRs@SiO$_2$ in mixed solution was plotted against with refractive index, as shown in Fig. 5C. It was found that plasmon absorption shifts linearly to longer wavelength with increasing the refractive index. In addition, only absorption is considered here and the influence of scattering are neglected due to higher absorption than scattering of nanorods.
The slope indicated the refractive index sensitivities, as shown in Fig. 5D. The sensitivity values of Au NRs@SiO₂ with different thickness were ranged from 110 nm/RIU to 390 nm/RIU. The Au NRs@SiO₂ with 2 nm shell exhibited highest sensitivity approaching to 390 nm/RIU, which was much higher than that of previous reports (the reported highest value was 325 nm/RIU)22, 33, 50. The sensitivity of Au NRs@SiO₂ had intimate relation with the silica shell and reduced gradually with increasing the shell thickness, which agreed with the results in previous work22, 31. The sensitivity of Au NRs@SiO₂ with 2 nm or 5 nm shell was larger than the values of Au NRs and the Au NRs@SiO₂ with other thickness. Generally, the improvement in sensitivity can be explained according to the universal experienced formula50–53

\[ \Delta \lambda = m(n_{\text{adsorbate}} - n_{\text{medium}})(1 - e^{-\frac{2d}{l_{\text{e}}}}) \]  

\( \Delta \lambda \) is the difference of the LSPR wavelength before and after coating; \( m \) is the sensitivity; \( n_{\text{adsorbate}} \) and \( n_{\text{medium}} \) are the refractive indexes of the shell and the solution, respectively; \( d \) is the thickness of the coating shell and \( l_{\text{e}} \) is the electromagnetic field decay length of the system, make \( A \) equal to \( (1 - e^{-\frac{2d}{l_{\text{e}}}}) \).

Figure 3. TEM images of Au NRs@SiO₂ with different shell thickness. The thickness of silica were as follows, respectively: (a) 2 nm; (b) 5 nm; (c) 10 nm; (d) 15 nm; (e) 20 nm; (f) 25 nm.

Figure 4. (A) Normalized extinction spectra of Au NRs@SiO₂ with different shell thickness from 2 nm to 20 nm; (B) Linearity curve of plasmon shift vs. the thickness of silica.
When Au NRs coated with thin silica, the change of A was ignored due to the minor change of d. The sensitivity was determined by the value of $\Delta \lambda / \Delta n$, which resulted in higher sensitivity than Au NRs due to higher change of $\Delta \lambda$ than $\Delta n$. However, when the silica shell became much thicker, the change of d can’t be ignored, which resulted in the increase of A. Though the value of $\Delta \lambda$ increased, the sensitivity decreased following the increase of $\Delta n$ and A. Therefore, it is not uncommon that the Au NRs@SiO$_2$ with 2 nm shell was with the highest sensitivity for about 390 nm/RIU.

Au NRs@SiO$_2$ with 2 nm of shell thickness showed optimal sensitivity of 390 nm/RIU and can serve as ideal candidate for high-efficiency LSPR sensors. Au NRs@SiO$_2$ was modified with specific antibody to selectively detect E. coli O157:H7. Due to the negative shell, the surface of the Au NRs@SiO$_2$ was negatively charged, which provided opportunity for the electrostatic interaction between Au NRs@SiO$_2$ and the positive antibody (Fig. S2) and simplified the procedure and avoided extra chemical treatment. E. coli O157:H7 samples with different concentration were mixed with antibody-conjugated Au NRs@SiO$_2$ to promote the sufficient incubation. Then the typical plasmon band shifts of Au NRs were measured using UV-vis absorption spectra to detect E. coli O157:H7 (Fig. 6A). After integrated with E. coli O157:H7, the longitudinal plasmon band of Au NRs@SiO$_2$ redshifted gradually and the absorption intensity was decreased gradually when increasing the concentration of E. coli O157:H7 in the range from 0 to $0.5 \times 10^5$ CFU (Fig. 6A).

Au NRs@SiO$_2$ was sensitive to the surrounding refractive. With increasing the concentration of E. coli O157:H7, the refractive index around Au NRs@SiO$_2$ increased, which led to the redshift of the longitudinal plasmon band$^{24}$. The relationship between plasmon band shift and logarithmic concentration of E. coli O157:H7 is shown in Fig. 6B. It was found that the redshift changed linearly with the logarithmic concentration of E. coli O157:H7, which made it possible to detect E. coli O157:H7 quantitatively. Furthermore, the experiment of the selectivity of the sensor had been done by using Salmonella Typhimurium (S. Typhimurium) with the antibody of E. coli O157:H7 (Fig. S3) to replace E. coli O157:H7. The LSPR band of Au NRs@SiO$_2$ was almost unchanged except some negligible change (around 0.5 nm). The results indicated that the antibody-conjugated Au NRs@SiO$_2$ only bind to E. coli O157:H7 due to the specific recognition.

Conclusion

In summary, a highly sensitive plasmon resonance biosensor based on Au NRs@SiO$_2$ was prepared to detect E. coli O157:H7 quickly and simply. By adjusting the concentration of CTAB and the amounts of TEOS, we
synthesized monodisperse Au NRs@SiO$_2$ with serious uniform silica shell. Meanwhile, the refractive index sensitivities of both Au NRs and Au NRs@SiO$_2$ with different thickness of silica shell were investigated and the Au NRs@SiO$_2$ with 2 nm shell was most sensitive compared to others. In addition, the Au NRs@SiO$_2$ with 2 nm shell was used here to detect the _E. coli_ O157:H7 by simply physical adsorption between antibodies and Au NRs@SiO$_2$. The results indicated that the plasmon shift was very sensitive to the change of the concentration of _E. coli_ O157:H7 and monitoring _E. coli_ O157:H7 at concentration lower than 10 CFU in less than 40 min, which meant the LSPR platform based on Au NRs@SiO$_2$ was sensitive, simple, quick for monitoring _E. coli_ O157:H7 without any expensive instruments and this label-free method was promising to applied in detecting pathogenic agents.

**Methods**

**Reagents and materials.** Hexadecyltrimethylammonium bromide (CTAB), Sodium borohydride (NaBH$_4$) and Tetraethylorthosilicate (TEOS) were commercially available from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). L-Ascorbic Acid (AA) was purchased from Energy Chemical in Shanghai. Chloroauric acid (HAuCl$_4$$\cdot$3H$_2$O, 99.9%), Silver nitrate (AgNO$_3$), ethanol, hydrochloric acid (HCl) and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). _E. coli_ O157:H7 (1.7$\times$10$^8$ CFU/mL), _Salmonella Typhimurium_ (S. Typhimurium) (2.48$\times$10$^8$ CFU/mL) and the murine anti- _E. coli_ O157:H7 monoclonal antibody were purchased from Meridian Life Science, Inc. (Memphis, TN). Phosphate buffer saline (PBS, pH = 7.4) was purchased from Sigma Chemical Company (St. Louis, MO) and was used to dilute the _E. coli_ O157:H7 stock solution (1.7$\times$10$^8$ CFU/mL) with different concentrations (from 10 to 10$^5$ CFU/mL). Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and used without any further purification.

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100F instrument and operated at 200 kV. Scanning electronic microscopy (SEM) measurements were carried out by a JEOL JMS-6700F scanning microscope. UV-vis absorption spectra were collected by virtue of TU-1810 UV-vis spectrophotometer provided by Purkinje General. The surface zeta potential data was performed on a Zeta Potential Analyzer.

**The Synthesis of Gold Nanorods.** CTAB stabilized gold nanorods were synthesized using the seed-mediated growth method with minor modifications.$^{36,34}$ First, 0.6 mL of freshly prepared ice-cold aqueous NaBH$_4$ solution (0.01 M), was added into mixed aqueous solution containing 0.25 mL, 0.01 M HAuCl$_4$ and 9.75 mL, 0.1 M CTAB. After string violently for 2 min, the seeds formed and were used within 10~120 min. The growth solution was prepared by mixing the aqueous solution of 4 mL, 0.01 M HAuCl$_4$, 0.8 mL, 0.01 M AgNO$_3$, 80 mL and 0.1 M CTAB firstly. Then 0.64 mL, 0.1 M freshly prepared aqueous ascorbic acid solution was added into the above mixture solution with gentle string, followed by adding 1.6 mL, 0.1 M HCl aqueous solution. After mixing the resultant solution with gentle string, 0.02 mL seed solution was added then mixing it with gentle inversion for 10 s and then left the growth solution undisturbed at least 6 h.

**The synthesis of Au NRs@SiO$_2$ with different thicknesses.** The synthesis of Au NRs@SiO$_2$ with homogeneous silica thickness was carried out according to the traditional soft-templating method.$^{35}$ The 10 mL of as-prepared Au NRs was washed using deionized water by centrifugation (6500 rpm, 10 min) for 2 times. The supernatant was removed and the pellet was diluted to 10 mL by adding deionized water. Then a certain amount of NaOH (0.1 M) was added to the above solution to adjust the solution PH to 10.6. After the solution was mixed for 20 min, three 2$\mu$L, 4$\mu$L, 6$\mu$L, 10$\mu$L, 15$\mu$L, 20$\mu$L injections of 20% TEOS in ethanol solution was added under gentle stirring at 30 min intervals and the solution was mixed under room temperature for 24 h.

**Refractive Index Sensitivity Measurements.** Water/glycerol solutions with a percentage of glycerol ranging from 0 to 90% at 10% intervals were used to change the refractive index experienced by the Au NRs and Au NRs@SiO$_2$. The refractive indexes were calculated according to the Lorentz-Lorenz equation as follows:

$$\text{Figure 6.} \quad (A) \quad \text{UV-vis spectra of Au NRs@SiO}_2 \text{ after reaction with different concentrations (from 0 to 0.5 × 10}^6 \text{ CFU) of } E. \text{ coli O157:H7 in the 0.01 M PBS solutions (pH = 7.4);} \quad (B) \quad \text{Linearity curve for the plot of plasmon shift vs. the logarithm of concentration of } E. \text{ coli O157:H7 (n = 1, 2, 3, 4, 5, 6).}$$
\[
\frac{n_2^2 - 1}{n_2^2 + 2} = \frac{\varphi_2^2}{n_2^2 + 2} + \frac{\varphi_3^2}{n_2^2 + 2}
\]

Wherein \(n_2\) is the refractive index of the mixture, \(n_1\) (1.3334) and \(n_2\) (1.4746) are the refractive indices of water and glycerol, respectively, \(\varphi_2\) and \(\varphi_3\) are their volume fractions. For sensitivity measurements, 3 mL particle samples in solvent with different concentration of glycerol were used. The location of the absorption peak changed response to the concentration variety of glycerol. The LSPR shift showed linearly dependence on the refractive index change and the slope represented the sensitivity of the corresponding sample.

**Immiscibility of antibodies on Au NRs@SiO2 and Detection of E. coli O157:H7.** Firstly, 5 mL of as-prepared Au NRs@SiO2 was washed for 2 times by centrifugation (6500 rpm, 6 min) and redispersed into 5 mL PBS solution (pH 7.4, 0.01 M). Then 1 mL 0.1 μg mL⁻¹ antibodies for E. coli O157:H7 was added into the above solution and stirred for 30 min at room temperature. Then the antibodies conjugated Au NRs@SiO2 was centrifuged for once to remove free antibodies and redispersed into 5 mL of PBS (pH 7.4, 0.01 M). 0.5 mL E. coli O157:H7 with different concentrations were mixed with 0.5 mL the as-synthesized antibodies conjugated Au NRs@SiO2. After gentle shaking for 10 min, the mixture was settled for 70 min without disturbance at 37°C. Then the resultant solution was detected under UV-vis measurement. The selective experiment was similar to the above detecting experiment just replaced the E. coli O157:H7 with S. Typhimurium of equal volume.

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Author Contributions
L.-P. S., Y.-J. H. and Z.-D. X. designed the research; L.-P. S. and L. Z. performed the experiments; L.-P. S., L. Z., L.-M. C. and G.-G. Z. analyzed the data; Y.-J. H., Z.-Y. S., J.-W. Z., Z.-D. X. and T. C. contributed to the reagents/materials/analysis tools; L.-P. S., L. Z. and Y.-J. H. wrote the paper; All authors approved the final manuscript.

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