

Layer by layer polyelectrolyte encapsulation of satellite structured Fe₃O₄@SiO₂-Au magnetic SERS probe for selective detection of food dyes

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ABSTRACT

Surface-enhanced Raman scattering (SERS) is a rapid and ultrasensitive spectroscopic technique in chemical analysis. We synthesized Au NPs with a tunable loading density on magnetic Fe₃O₄@SiO₂ bead to form a core-satellite Fe₃O₄@SiO₂-AuNPs (FA) hetero-nanostructure via layer by layer polyelectrolyte encapsulation method. Adsorption experiments indicate the SERS substrate could selectively capture the analyte around its “hot spots” regions and subsequently enhance its Raman signal. This magnetic SERS substrate was also successfully applied in detecting food dyes in commercial beverages. As a result, this SERS platform provides an easy and fast screening technique for in situ analysis of food dye molecules with charge.

Keywords: Layer by layer, food dye, selective detection, polyelectrolyte, SERS

1 INTRODUCTION

Taking advantage of the explosive growth in nanofabrication, great efforts have been made in the attempt to synthesize SERS-active noble metal nanoparticles (NPs) with tunable size, shape, and functionality. Among these substrates, functionalized core-shell magnetic nanoparticles have recently been used for highly sensitive SERS detections¹.

Synthetic food dyes are widely used in food manufacturing and might exert adverse effects on human health after excessive consumption. SERS techniques also have been applied to foods contaminants since the late 1990s, mainly driven by the need for a rapid and sensitive detection tool. An intrinsic difficulty to analytical chemists is selective separating trace amounts of analytes from complex matrices cause of background interference, and this difficulty is also a factor in SERS implementation.

The objective of the study is, therefore, to provide a potential application platform for selective capture and detection of food dyes in real word matrices. We synthesized multifunctional FA satellite structured system via layer by layer (LBL) method as SERS substrate for selective food dyes detection. We observed that the multifunctional FA satellite system exhibit excellent charge selectivity.

2 EXPERIMENTAL SECTION

2.1 Materials

All reagents were of analytical reagent grade and used without further purification. HAuCl₄·4H₂O, NaCl, Ferric chloride hexahydrate (FeCl₃·6H₂O), trisodium citrate dehydrate and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Tetraethyl orthosilicate (TEOS), poly-(diallyldimethyl ammonium chloride) (PDDA, Mw 200000~350000, 20% in H₂O), poly-(styrene sulfonate) (PSS, Mw ~70000, 30% in H₂O), Malachite Green (MG) was from Aldrich Scientific Ltd. (China). Sunset Yellow(SY) and Indigo were from Tokyo Chemical Industry Co., LTD. Absolute ethanol, ethylene glycol (EG) (>99.7%) were from Beijing Chemical Reagents Company (China). Milli-Q water (>18.2MΩ) was used in all experiments. The stock solution of HAuCl₄ (2 wt.% in water) was prepared by dissolving HAuCl₄·4H₂O.

2.2 Synthesis of SERS selective FA satellite structured nanocomposites

The citrate-stabilized Au NPs were synthesized by modifying the reported procedure.² The magnetic Fe₃O₄ nanoparticles were synthesized via a solvothermal reaction according to a previous report.³ Briefly, FeCl₃·6H₂O (2.70 g) and NaAc (7.2 g) were dissolved in ethylene glycol (100 mL) with magnetic stirring at room temperature for 1 h. The homogeneous yellow solution was then transferred into a Teflon-lined stainless-steel autoclave and sealed to heat at 200 °C. After reaction for 12 h, the autoclave was cooled to room temperature. The obtained Fe₃O₄ NPs were washed with ethanol and d water three times respectively, and then dried under vacuum at 60°C for 3 h. The synthesis of core-shell Fe₃O₄@SiO₂ microspheres were carried out according to the noted Stöber method with a little modification.⁴ Typically, 0.2 g of magnetic microspheres was pretreated with 0.1 M HNO₃ aqueous solution under ultrasound for 10 min, followed by washing with water. Then, the treated Fe₃O₄ microspheres were redispersed in a mixture of 20 mL of ethanol and 4 mL of water by ultrasonication for another 10 min. Then under continuous mechanical stirring, 1 mL of ammonia solution (25%) and 0.8 mL of tetraethyl orthosilicate (TEOS) were consecutively added to the

mixture. The reaction was allowed to proceed at room temperature for 3 h under continuous stirring. The resulting products were collected and washed, and then dried under vacuum at 60 °C for 2 h for further use. FA magnetic microspheres were prepared via a LBL assembly approach.⁵ A colloidal suspension of Fe₃O₄ (100mg in 1 mL water) was added to 99 mL of PDDA solution (2%, contained 20×10⁻³ M trisodium citrate and 20×10⁻³ M NaCl) under mechanical stirring for 1h. Residual PDDA was removed with the help of a magnet and the PDDA adsorbed microspheres were washed with water at least six times. The resulting magnetic microsphere (10 mg) were redispersed in gold colloid (1-30 mL) and the mixture was shaking for 20 min (30°C, 150 r/min). The resulting FA nanocomposite was isolated with a magnet and washed three times by water. It was dispersed again in water for the following experiment. To fabricate positive charged FA-PDDA(+), FA (10 mg) were dispersed in 10 mL PDDA solution (2%, contained 20×10⁻³ M trisodium citrate and 20×10⁻³ M NaCl) and the resulting dispersion was shaking for 20 min (30°C, 150 r/min). Residual PDDA was removed with the help of a magnet and the FA-PDDA(+) microspheres were rinsed with water at least six times. To modify the surface charge of FA-PDDA(+) from positive to negative. The microspheres were further decorating with anion PSS. The FA-PDDA(+) magnetic microspheres (10 mg) were dispersed in 10 mL PSS solution (3%, contained 20×10⁻³ M NaCl) and the resulting dispersion was shaking for 20 min (30°C, 150 r/min). Residual PSS was removed with the help of a magnet and the FA-PSS(-) microspheres were rinsed with water at least six times.

The distribution, morphology, zeta potential and magnetic properties of Fe₃O₄@SiO₂-Au were characterized through high-resolution transmission electron microscopy (HR-TEM, JEM-2010, JEOL), field emission scanning electron microscopy (FESEM, SU-8020, Hitachi), vibration sample magnetometer (VSM, LDJ9600, Troy, MI), Malvern Zetasizer Nano ZS (Malvern Instruments, U.K.).

2.3 Adsorption of dyes by FA

The Fe₃O₄@SiO₂-Au/FA-PDDA(+)/FA-PSS(-) (1 mg) were added to 1mL of malachite green/Sunset yellow/indigo solutions (50 mM), each taken in separate 2 mL centrifuge tube. The mixture was shaken at room temperature for 1 h. The samples were magnetic collected and the dye solution was measured using a spectrophotometer (UV-2550 Shimadzu). Each experiment was performed five times.

2.4 SERS detection of dyes on FA satellite structured nanocomposites

The mixture samples of SY, Indigo, and MG were prepared by diluting the stock solution in DI water to reach a final concentration of 5×10⁻⁵ M for each dye. The FA/FA-PDDA(+)/FA-PSS(-) substrate (0.2 mg) was immersed in a

1 mL solution containing various concentrations of dyes for 5 min. For the analysis of the soft drink purchased from the market, FA-PDDA(+) substrate (1mg) was immersed in 1 mL of beverage for 5 min. Then, the microspheres were assembled by an applied magnetic field and washed by water, and exposed to the laser to measure the SERS signal.

3 RESULTS AND DISCUSSION

3.1 Layer by layer synthesis of FA satellite structure

The FA satellite structure was prepared through LBL assembly process. The Fe₃O₄ microspheres with a mean diameter of 370 nm are wrapped in a SiO₂ shell having a thickness of about 60 nm. Negatively charged Fe₃O₄@SiO₂ beads (-48 mV) were wrapped with cationic polyelectrolyte PDDA (43 mV) to form an ultra thin layer with a homogeneous distribution of positive charges. The cationic PDDA acts as a bridge for the connection between AuNPs (-19 mV) and silicon shell. Thus, uniformly distributed Au NPs were assembled on each Fe₃O₄@SiO₂ bead to form core-satellite FA hetero-nanostructure (Figure 1A, 1B). The maximum saturation magnetizations value of Fe₃O₄ microspheres is measured at 76 emu·g⁻¹. Although the addition of nonmagnetic silicon leads to a decreased of saturation magnetizations, the obtained Fe₃O₄@SiO₂ microspheres still have a high saturation magnetization of 41 emu·g⁻¹. After further depositing of Au shell, no value decrease was observed. According to Ma's study, a saturation magnetization of 16.3 emu·g⁻¹ is enough for magnetic separation from solution with a magnet.⁶

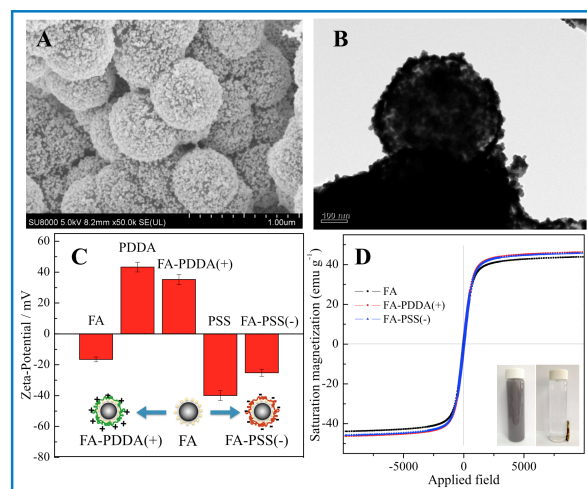


Figure 1: SEM (A) and TEM (B) images of satellite structured Fe₃O₄@SiO₂-Au. (C) Evolution of Zeta-potentials during the LBL FA functional processes.(The insets show schematic illustration of tunable charge functional of core-satellite FA hetero-nanostructure.) (D) Magnetic hysteresis loops of Fe₃O₄, Fe₃O₄@SiO₂ and FA

microspheres. (The insets show their suspensions before and after magnetic separation by an external magnet).

PDDA is a positively charged polymer due to the presence of amino groups. Therefore, PDDA can be strongly attracted to negatively charged FA (-18 mV) through electrostatic interaction to form positively charged FA-PDDA(+)(Figure 1C). Then FA-PDDA(+) could easily combine with sulfate groups of PSS in aqueous solution to form negatively charged FA-PSS(-). The Zeta potential values of FA-PDDA(+) and FA-PSS(-) were measured to be +35 mV and -25 mV (Fig. 1C), respectively, confirmed the successful modification of FA structure with desirable charge. Moreover, further charge functionalization has no obvious influence on the magnetic properties of FA nanocomposites (Figure 1D). Thus, the resulting multifunctional FA-PDDA(+)/FA-PSS(-) magnetic nanocomposites not only provide a platform for selectively enriching the electroactive charged molecular, but also provide an effective means for the dye separation from samples via application of a magnetic field.

3.2 Selective detection of food dyes by FA satellite structured nanocomposites

As shown in Figure 2, we proposed that the negatively charged analyte (i.e., Malachite Green) should preferentially adsorb on the positively charged substrate and its Raman signal be substantially enhanced due to the SERS effect of gold (Au) NPs. Similarly, positively charged analyte (i.e., Sunset Yellow) could be enriched on the negatively charged substrate and then be detected by portable Raman detector.

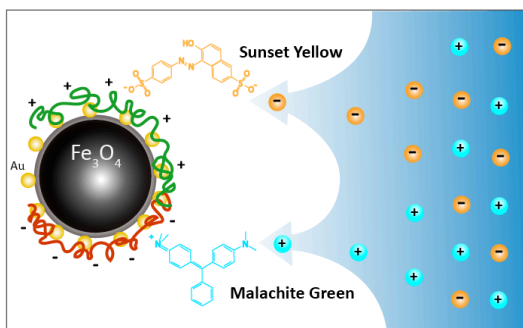


Figure 2: Schematic illustration of the selective adsorption and detection of analyte on FA SERS substrate.

As shown in Figure 3, the SERS signal of negatively charged sunset yellow, SY(-), was appreciably elevated on the positively charged FA-PDDA(+) substrate. The obtained enhancement factor (10^4) is in the same level as a previous report.⁷ In contrast, no SERS enhancement was detected on this positive substrate for malachite green, MG(+), and indigo (neutral charge) (Figure 3A). Similarly, negatively charged FA-PSS(-) substrate selectively increased the SERS signal of positively MG(+), but not the

other two (Figure 3B). The adsorption experiments indicated that the functionalized substrate is favorable for the uptake of opposite charged dyes with the adsorption capacity of over 91%. This high affinity facilitates the SERS substrate to selectively capture analyte around its “hot spots” regions which subsequently enhance its Raman signal. This magnetic SERS substrate was also successfully applied in detecting food dyes in commercial beverages. As a result, this SERS platform provides an easy and fast screening technique for in situ analysis of food dyes and molecules with charge.

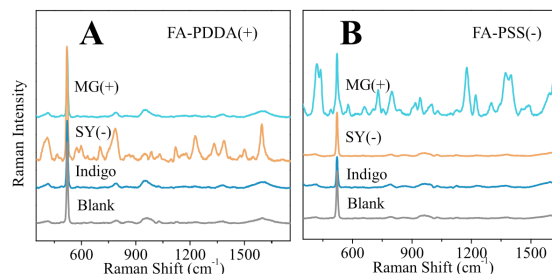


Figure 3: Selective SERS detection of food dyes on positively charged PDDA-FSPA (C) and on negatively charged PSS-FSPA (D).

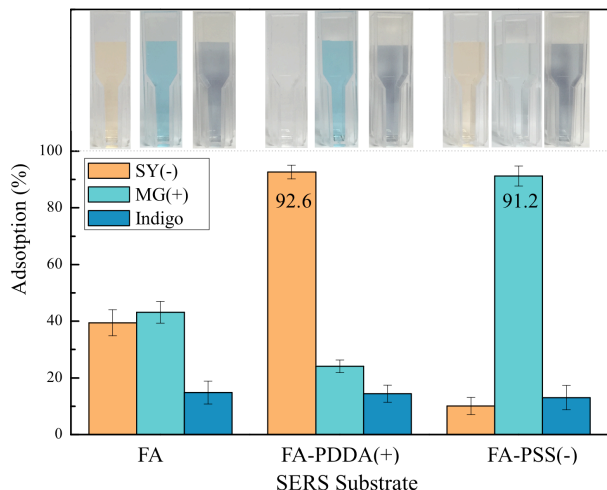


Figure 4: Adsorption capacity of FA, FA-PDDA(+) and FA-PSS(-) for SY(-), MG(+) and Indigo. The data points represented the average \pm standard deviation for 3 times. The inset photograph shows the dye color change with the existence of each substrate.

To understand the selective detection of food dyes, the adsorption experiment was performed. The absorption peaks at 618, 484 and 699 nm can be used to monitor the MG, SY and In contents respectively. The adsorption of dye can be demonstrated by the decrease of maximum UV-vis adsorption (A_{max}) intensity. A sharp decrease in the A_{max} intensity accompanied by significant color change of dye solution was completed within 5 min with the exist of opposite charged substrate, indicating that the charge selective FA substrate is more favorable for dye adsorption

than other substrate. The adsorption efficiency for SY and MG can reach above 92.6% and 91.2 respectively (Figure 4). This result creates favorable conditions for functional substrate to capture analytes around its “hot spots” region, and then SERS selective detection was realized.

3.3 SERS detection of food dyes in real world matrices on FA substrate

To test the selectivity of the charge tunable substrate from a chemical mixture, FA-PDDA(+) and FA-PSS(-) substrate was separately exposed to a mixture solution of SY(-), MG(+) and Indigo (concentration of 5×10^{-5} M each). Following thorough rinsing with DI water, SERS spectra were collected from both substrate. The FA-PSS(-) exhibited Raman bands corresponding to MG(+) while the FA-PDDA(+) exhibited Raman bands corresponding to SY(-) (Fig. 5A).

To elucidate the charge selectivity of substrate with varying chemical and physical environmental conditions, FA-PDDA(+) was also exposed to chemically complex media involving many interfering compounds. For example, beverage represents a complex mixture of organic chemicals, especially anionic dye, such as sunset yellow. Figure 5D clearly shows the prominent characteristic Raman bands of SY(-) detected from FA-PDDA(+). The stability results illustrated that the FA-PDDA(+) substrate can be applied in monitoring of food dye in commercial beverage with obvious sensitivity in 79 days. These results clearly indicate the charge selectivity of polyelectrolyte-modified FA even in real system.

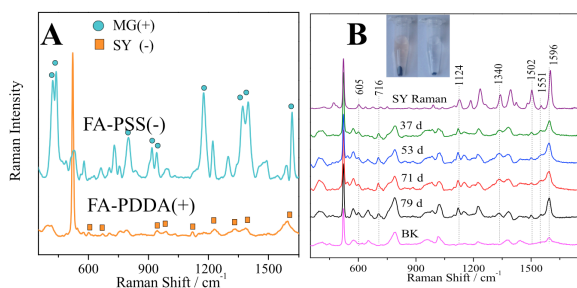


Figure 5: (A) SERS spectra of FA-PDDA(+)/PSS(-) substrate for the mixture solution of 5×10^{-5} M SY, 5×10^{-5} M MG and 5×10^{-5} M Indigo. Signal collecting time = 5 s. (B) SERS spectra of FA-PDDA(+) for SY contained beverage within 79 days. The inset photograph shows the beverage color changed with the existence of FA-PDDA(+) substrate.

4 CONCLUSION

Au NPs were uniformly deposited on magnetic $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ bead to form a core-satellite FA hetero-nanostructure with tunable loading density via LBL polyelectrolyte encapsulation method. Further LBL

decoration of charged polyelectrolyte outside satellite structure induced a greater adsorption and selectivity in SERS detection of negatively(-) and positively(+) charged food dye molecules. Adsorption experiments indicated that the charged substrate is favorable for the uptake of opposite charged dyes with an adsorption capacity over 91% as evidenced by the molecular dynamic simulation. This high affinity facilitates the SERS substrate to selectively capture the analyte around its “hot spots” regions and subsequently enhance its Raman signal. This magnetic SERS substrate was also successfully applied in detecting food dyes in commercial beverages. The sensitivity of this analytical method have opened a new way toward a generalized use of SERS technique, not only in the laboratory but also in field assays with a portable Raman spectrometer.

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