Multifunctional $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--Au}$ Satellite Structured SERS Probe for Charge Selective Detection of Food Dyes

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S Supporting Information

ABSTRACT: Nanofabrication of multifunctional surface-enhanced Raman scattering (SERS) substrates is strongly desirable but currently remains a challenge. The motivation of this study was to design such a substrate, a versatile core–satellite $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--Au}$ (FA) hetero-nanostructure, and demonstrate its use for charge-selective detection of food dye molecules as an exemplary application. Our experimental results and three-dimensional finite difference time domain (FDTD) simulation suggest that tuning the Au nanoparticle (NP) gap to sub-10 nm, which could be readily accomplished, substantially enhanced the Raman signals. Further layer-by-layer deposition of a charged polyelectrolyte on this magnetic SERS substrate induced active adsorption and selective detection of food dye molecules of opposite charge on the substrates. Molecular dynamics (MD) simulations suggest that the selective SERS enhancement could be attributed to the high affinity and close contact (within a 20 Å range) between the substrate and molecules. Density function theory (DFT) calculations confirm the charge transfer from food dye molecules to Au NPs via the polyelectrolytes. This multifunctional SERS platform provides easy separation and selective detection of charged molecules from complex chemical mixtures.

KEYWORDS: SERS, tunable gap, selective detection, food dye, charge transfer

INTRODUCTION

Plasmonic core–satellite structures have promoted the application of surface-enhanced Raman scattering (SERS) in chemical analysis.^{1–9} However, most of these structures are limited to a single use or single function. Taking advantage of the explosive growth in nanofabrication, the exploitation of multifunctional nanoassemblies, including plasmonic core–satellite structures, has caused increasing interest in integrating novel optical, charge selective, and magnetic properties.^{10–12}

To date a few studies have attempted to improve the SERS selectivity based on the use of n- or p-type Si wafer substrates for positively or negatively charged dye molecules.^{13,14} Although this approach could achieve selective SERS detection of dyes, a more efficient process is desirable to promote the active capture of target analytes in the presence of interfering species. To this end, Tian et al. implemented polyelectrolyte-coated gold nanorods on filter paper as a selective SERS substrate to detect positively (rhodamine 6G) and negatively (methyl orange) charged analytes.¹⁵ Meanwhile, Zhu et al. used polyelectrolyte-decorated Ag nanoparticle (NP) based filter paper for the rapid separation, preconcentration, and SERS detection of colorants in drinks with complex components.¹⁶

The motivation for our study was to fabricate multifunctional magnetic satellite-structured $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{--Au}$ (FA) substrates

with tunable Au NP gaps for active capture and charge selective SERS analysis of food dyes. Layer-by-layer (LBL) assembly is known as a highly versatile method for the fabrication of layered structures from various components in a simple, inexpensive, and rapid procedure.^{17–20} It has been used to assemble various materials, including NPs, cells, nanotubes, proteins, DNA, and RNA. Thus, this flexible LBL assembly approach is promising for the preparation and functionalization of materials, such as magnetic core–satellite structures.

The synthetic dyes, such as sunset yellow, were often abused because of their low price.²¹ Their excessive intake can cause adverse health impacts, such as allergy, skin itching, and bronchial asthma symptoms.²² Therefore, there is an urgent need for in situ determination of synthetic dyes. Our previous reports have demonstrated the advantages of magnetic $\text{Fe}_3\text{O}_4@\text{Ag}$ as SERS substrates in detecting environmental pollutants.^{23,24} To improve the chemical stability and versatile functionality of the substrate, we propose to use FA with further LBL assembly. Herein, we fabricated $\text{Fe}_3\text{O}_4@\text{Au}$ by grafting Au NPs onto micro-sized Fe_3O_4 . The core–shell-

Received: October 25, 2015

Accepted: January 13, 2016

Published: January 13, 2016

satellite 3D magnetic microspheres can create sufficient hotspots between the $\text{Fe}_3\text{O}_4@\text{Au}$ core and assembled Au satellites. The results of adsorption experiments, three-dimensional finite difference time domain (FDTD) simulation, molecular dynamics (MD), and density function theory (DFT) calculation suggest that the electrostatic forces enable the SERS substrate to selectively capture the analyte around its “hot spots” regions, which induces charge transfer and subsequently enhances its Raman signal.

EXPERIMENTAL SECTION

Chemicals and Materials. All reagents were of analytical grade and used without further purification. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, NaCl, ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), trisodium citrate dehydrate, and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Tetraethyl orthosilicate (TEOS), poly-(diallyldimethylammonium chloride) (PDDA, $M_w = 200000$ – 350000 , 20% in H_2O), poly(styrenesulfonate) (PSS, $M_w = \sim 70000$, 30% in H_2O), malachite green (MG), congo red, and crystal violet were from Aldrich Scientific Ltd. (China). Sunset yellow (SY), indigo, and allure red were from Tokyo Chemical Industry Co., Ltd. Amazon orange G was from Tianjin Biochem LLC. Ammonia aqueous solution, absolute ethanol, and ethylene glycol (EG) (>99.7%) were from Beijing Chemical Reagents Company (China). Milli-Q water (>18.2 M Ω) was used in all experiments. The stock solution of HAuCl_4 (2 wt % in water) was prepared by dissolving $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$.

Fabrication of FA-Satellite Structure. The citrate-stabilized Au NPs were synthesized by modifying a reported procedure.²⁵ Briefly, a total of 2 mL of HAuCl_4 (2 wt %) was added to 46 mL of H_2O in a three-neck flask and heated to 100 °C in an oil bath with stirring. Then, 2 mL of sodium citrate (100 mg) was quickly added to the above solution. The mixture was reacted for 20 min at 100 °C. The resulting colloid was cooled to room temperature under vigorous stirring.

The magnetic Fe_3O_4 nanoparticles were synthesized via a solvothermal reaction according to a previous report.²⁶ Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (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, sealed, and heated at 200 °C. After reaction for 12 h, the autoclave was cooled to room temperature. The obtained Fe_3O_4 NPs were washed first with ethanol then DI water (three times each), and then dried under vacuum at 60 °C for 3 h.

The synthesis of core-shell $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres was carried out according to the noted Stöber method with a minor modification.²⁷ Typically, 0.2 g of magnetic microspheres were retreated with 0.1 M HNO_3 aqueous solution under ultrasound for 10 min, followed by washing with DI water. Then, the treated Fe_3O_4 microspheres were redispersed in a mixture of 20 mL of ethanol and 4 mL of DI 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.²⁸ A colloidal suspension of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (100 mg in 1 mL of water) was added to 99 mL of 2% PDDA solution containing 2×10^{-2} M trisodium citrate and 2×10^{-2} M NaCl under mechanical stirring for 1 h. The excess PDDA on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres was removed with the help of a magnet and the PDDA-adsorbed microspheres were washed with water at least six times. The resulting magnetic microspheres (10 mg) were redispersed in Au colloids (1–30 mL) and the mixture was shaken for 20 min (30 °C, 150 r min⁻¹). 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.

Polymer Modification. To fabricate positive charged FA-PDDA(+), FA (10 mg) were dispersed in 10 mL of PDDA solution (2%, contained 2×10^{-2} M trisodium citrate and 2×10^{-2} M NaCl), and the resulting dispersion was shaken for 20 min (30 °C, 150 r min⁻¹). 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 decorated with anionic PSS.²⁹ The FA-PDDA(+) magnetic microspheres (10 mg) were dispersed in 10 mL of PSS solution (3% in 2×10^{-2} M NaCl) and the resulting dispersion was shaken for 20 min (30 °C, 150 r min⁻¹). Residual PSS was removed with the help of a magnet and the FA-PSS(−) microspheres were rinsed with water at least six times.

Sample Preparation for SERS Analysis. The samples of SY, indigo, and MG and their mixture were prepared by diluting the stock solutions 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 (1 mg) was immersed in 1 mL of beverage for 5 min. Then, the microspheres were assembled by an applied magnetic field and washed with water, and exposed to the laser for 5 s to measure the SERS signal.

Apparatus. The ultraviolet–visible (UV–vis) spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The absorption peaks at 619, 484, and 699 nm can be used to monitor the MG, SY, and Indigo contents, respectively.^{30,31} The adsorption of dye can be demonstrated by the decrease in maximum UV–vis adsorption (A_{max}) intensity. TEM images and elemental mapping of FA were characterized using high-resolution transmission electron microscopy (HR-TEM, JEM-2010, JEOL). The surface morphology of the FA was obtained using field emission scanning electron microscopy (FESEM, SU-8020, Hitachi). Magnetic properties were measured by a vibrating sample magnetometer (VSM, LDJ9600, Troy, MI). Zeta potential measurements were carried out on a Malvern Zetasizer Nano ZS (Malvern Instruments, U.K.). Raman spectra were obtained using a portable Raman spectrometer (Enwave Optronics, Inc. USA) with a 4 cm⁻¹ resolution at the excitation energy of 785 nm, and adjustable power with a maximum at 300 mW.

FDTD Calculations. The distribution of electromagnetic field intensity around the FA nanostructures was calculated using the FDTD method. The FDTD Solutions software package (Lumerical Solutions Inc., Vancouver Canada) was used to carry out the computational calculations and numerical analysis. The mesh size was 1 nm. The calculation time was 1000 fs. A $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core surrounded by varying density of satellite Au NPs was calculated. The distance between the core and its satellites was set to 0 nm.

MD Simulation. The sampling of all model systems was carried out using MD simulations. The MD simulations were performed using the Forcite module with the universal force field in Materials Studio (Accelrys, San Diego, CA). This is an accurate force field for the calculation of molecular interactions in aqueous solution and has been widely used in previous studies.³² A simple point charge (SPC) model was used to calculate the water molecules.³³ All initial solid/water interface configurations were energy minimized using the smart minimizer method before running the dynamics. This stepwise scheme entails steepest-descent switching to the conjugated gradient method as the energy derivatives decrease in order to accelerate the computation.³³ Equilibration and subsequent simulations were conducted under the canonical (NVT) ensemble with a time step of 1.0 fs. The system temperature was maintained at 298 K using the Nose thermostat. The velocity Verlet algorithm was used to integrate the equations of motion.³⁴ Initial velocities were randomly assigned according to a Boltzmann distribution,³⁵ then used as current. The Ewald summation method was used to calculate the electrostatic interactions,³⁶ and the atom-based summation method with a cutoff distance of 9.5 Å was chosen to handle the van der Waals interactions.³³ Each simulation for all studied systems was preceded by a pre-equilibration period of 100 ps and followed by 1000 ps to reach equilibrium.

Figure 1. SEM images of FA substrates with the Au distance of 61 (A1), 17 (A2), 12 (A3), and 7 nm (A4). B1–B4 show the distribution of Au NP gaps on samples A1–A4, respectively. The FDTD model is established with Au NP gaps at 60 (C1), 20 (C2), 10 (C3), and 5 nm (C4), and the model predicted electric field distributions with 785 nm excitation are presented in D1–D4.

Figure 2. (A) Zeta-potentials during the LBL FA charge functionalization. The insets sketch the tunable charge functionalization of core–satellite FA heteronanostructures. (B) Magnetic hysteresis loops of FA, FA-PDDA(+), and FA-PSS(−). The inset illustrates the magnetic separation by an external magnet.

DFT Simulations. DFT simulations were performed by the Dmol³ package in Materials Studio (Accelrys, San Diego, CA). The DNP double numerical basis set was used, in which the accuracy was comparable to the 6-31G** set. The core electrons were treated with effective core potentials. The exchange–correlation energy was calculated using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA).³⁷ A Monkhorst–Pack scheme with a $2 \times 1 \times 1$ k -point grid was employed to sample points over the Brillouin zone. A global orbital cutoff of 4.5 Å and a Fermi smearing of 0.005 Ha were employed during calculations. A self-consistent field tolerance of 1.0×10^{-6} Ha atom^{−1}, an energy tolerance of 1.0×10^{-5} Ha atom^{−1}, a maximum force tolerance of 0.002 Ha Å^{−1}, and a maximum displacement tolerance of 0.005 Å, respectively, were set as the convergence criteria for the geometric optimization and energy calculation. All atoms were allowed to relax during the optimization process.

RESULTS AND DISCUSSION

Multifunctional Satellite Structure. The FA satellite structure consisted of 20 nm Au NPs homogeneously deposited on Fe₃O₄@SiO₂, with tunable gaps among Au NPs ranging from 61 to 7 nm (Figure 1). The detailed fabrication process is described in the Experimental Section and shown in Figures S1 and S2. The FA satellite structure with uniform distribution was prepared through a LBL assembly process, as schematically illustrated in Figure S1A.

As a positively charged polyelectrolyte, PDDA was strongly attracted to the negatively charged FA (−18 mV) through electrostatic interactions and formed a positively charged FA-PDDA(+) complex (35 mV, Figure 2A). Then, FA-PDDA(+) could readily attract the negative PSS (−42 mV, Figure 2A) to

assemble the negatively charged FA-PSS(−) (−25 mV, Figure 2A). Importantly, this charge functionalization had no discernible impact on the magnetic properties of the FA satellite structures (Figure 2B). Thus, the resulting FA-PDDA(+)/PSS(−) magnetic nanocomposites may provide not only a platform for selectively enriching charged molecules, but also effective separation of an analyte from interfering matrices via the application of a magnetic field.

Tunable Au Interparticle Gaps. A major obstacle in the uniform fabrication of magnetic satellite spheres is the ability to template Au deposition with an uniform sub-10 nm precision. Herein, we fabricated the SERS substrate with different Au interparticle gaps by a LBL method as shown in the SEM image (Figure 1A). The NP distance was measured by randomly counting 500 gaps based on the SEM image using software Nano Measurer 1.2 (Figure S3). The distribution histogram of interparticle gaps (Figure 1B) resolved distances from 61 to 7 nm resulting from the addition of Au colloids from 1 to 30 mL in the FA preparation procedure.

As a result, the SERS intensity of SY(−), a negatively charged food dye, reached the maximum as the Au colloid addition increased from 1 to 10 mL (Figure 3). This increase in peak

Figure 3. Peak intensity of SY at 1596 cm^{-1} as a function of interparticle gaps between Au on PDDA-FA substrate. The gap distance was adjusted by tuning the volume (1–30 mL) of Au colloids. The solid points represent the average $\pm$ standard deviation at 25 randomly chosen points, signal collecting time = 5 s. The curves represent the standard deviation of interparticle gap distribution fitted by the GaussAmp model (Supporting Information).

intensity corresponded well to the gap distance of Au NPs narrowing from 61 to 12 nm, as evidenced by SEM images (Figure 1, A1–A3). When the volume of Au colloids increased beyond 10 mL, the SERS intensity reached a plateau (~ 1000 au) with Au interparticle gaps slightly decreasing to 7 nm (Figure 3). Notably, 7 nm might be the minimum Au NP gap this LBL approach could reach due to the repulsion between negatively charged Au NPs (−19 mV, Figure S1). Hence, a 7 nm gap created with addition of 30 mL of Au colloid was used for the subsequent experiments because the number and intensity of SERS “hot spots” appeared to be maximized on the substrate surface under these conditions (Figure 1A4).

Satellite structures with nanoscale gaps are highly desirable in optics and electronics. When irradiated with light, such structures are capable of producing up to $\sim 10^8$ electromagnetic field enhancement by confining the optical field to the sub-10 nm gap.^{4,7} The distribution of local electric field was further

simulated with FDTD methods to estimate the intensity as a function of the gap between Au NPs. FDTD simulation has been extensively used to study the optical properties of NPs in leading scientific publications^{38–41} because it considers complicated shape and size, which is essential to magnetic satellite structures. The FDTD results show that, in agreement with our SERS observations, the decrease in the Au NP gap from 60 to 5 nm was accompanied by elevation of the localized electromagnetic field (Figure 1C and 1D) because of effectively confined light in the Au cavities.⁴¹ If the wavelength of incident light matches the localized surface plasmon resonance of a metal nanostructure, a strong localized electromagnetic field will be excited in the vicinity of the nanogaps.^{42,43} Our FDTD model also predicts that the optimal SERS excitation wavelength for sub-10 nm gaps on FA satellite structures would lie in the red and near-infrared spectral region, such as 633 and 785 nm (Figure S4).

Charge Selective SERS Detection of Food Dyes. Negatively charged SY(−), neutrally charged indigo(0), and positively charged MG(+), were used as representative dye molecules to examine the SERS response of the FA satellite substrate. As shown in Figure 4A and B, the SERS signal of

Figure 4. SERS spectra of SY(−), MG(+), and indigo(0) on positively charged FA-PDDA(+) (A), and negatively charged FA-PSS(−) (B). SERS spectra of dye mixture containing SY(−), MG(+), and indigo(0) on FA-PDDA(+) and FA-PSS(−) substrate, respectively (C). SERS spectra of SY(−) on FA-PDDA(+) substrate in commercial beverage. The inset photograph shows the change in color in the presence of the FA-PDDA(+). The substrate was stored in DI water for up to 79 days (D). The concentration for each dye was 5×10^{-5} M. Signal collecting time = 5 s.

counter-charged molecules was appreciably elevated on the positively charged FA-PDDA(+) substrate. Specifically, the SERS spectrum exhibited strong Raman bands corresponding to SY(−) at $605, 716, 1124, 1340, 1502, 1551,$ and 1596 cm^{-1} on the positively charged FA-PDDA(+). The detection limit of SY(−) was 1×10^{-7} M (Figure S5), comparable to a previous report.⁴⁴ In contrast, no SERS enhancement was detected for molecules with no charge or with the same charge as the substrate (Figure 4A and B). This charge selectivity was further underlined in a mixture of MG(+), SY(−), and indigo(0)

Figure 5. Snapshots of the initial and final structures of dye molecules aggregated on different polyelectrolyte-modified Au surfaces. (A1, B1) SY-PDDA, (C1, D1) SY-PSS, (A2, B2) MG-PDDA, (C2, D2) MG-PSS, (A3, B3) indigo-PDDA, and (C3, D3) indigo-PSS side view. The water molecules were removed for clarity. Density distributions of dye molecules are shown as a function of distance from the PDDA surface (E) and PSS surface (F).

(Figure 4C). Though the PSS Raman characteristic peaks at 1124 and 1303 cm^{-1} were observable on the substrate with an intensity of about 400 au (Figure S6), its signal was substantially suppressed compared with the significant enhancement of the analyte (Figure 4).

Additional control experiments were performed to justify that dye molecules preferentially adsorb on the modified FA substrates rather than on the bare FA particles. The results in Figure S7A showed that the bare FA particles exhibited weak SERS enhancements for SY(−), MG(+), and indigo(0) with no selectivity. In contrast, the polymer modification endowed FA with high sensitivity and selectivity. For example, FA-PSS(−) exhibited a strong SERS enhancement toward MG (16789 au at 1172 cm^{-1} , Figure S7B), which is about seven times higher than unmodified FA (2441 au). The detection limit of 1×10^{-6} M using bare FA cannot meet the request for application due to the reduced SERS sensitivity in real environmental matrices (Figure S8). The results of control experiments confirm the preferential adsorption of dye molecules on modified FA substrates rather than on the bare FA particles, highlighting the importance of polymer modification for effect SERS enhancement.

To date, as far as we know, no report is available for simultaneous selective enrichment, magnetic separation, and SERS-based detection of multiple food dyes. We postulated that our multifunctional FA satellite substrate would be effective in concentrating and detecting negatively charged (i.e., allure red, congo red) and positively charged analytes (i.e., astrazon orange G, crystal violet), and this premise was clearly justified by our results, shown in Figure S9. To examine the applicability of this charge selectivity in complicated matrices, the functionalized FA satellite substrate was exposed to various pH conditions and commercial beverages. The change in pH from 3 to 9 did not significantly influence the surface charge of substrates and SERS response of food dyes (1×10^{-5} M, Figure S10 and 11). Meanwhile, Figure 4D clearly shows prominent

SY(−) Raman bands detected using FA-PDDA(+) in a beverage obtained from a local market. In addition, the stability results in Figure 4D illustrate that the FA-PDDA(+) substrate can be effectively applied in monitoring food dyes in commercial beverages after storage for 79 days.

MD Simulation. A prerequisite for SERS enhancement is that the dye molecules should be in close proximity to the substrate. Thus, the interaction of food dyes with FA-PDDA(+) and FA-PSS(−) was explored using MD simulation, and snapshots of initial and equilibrium states are illustrated in Figure 5. The results show that upon positive (PDDA) or negative (PSS) surface modification, only dye molecules with opposite charges could move close to the surface and be adsorbed at equilibrium (Supporting Information Video). The density profiles along the Z direction (i.e., normal to the Au surface) as shown in Figure 5E and F confirm the close contact of dyes (15–20 Å) with opposite charges to the surface due to electrostatic attractions.⁴⁵ This MD simulation is consistent with our experimental results showing that the adsorption of counter-charged dyes could be as high as 91.2–92.6% (Figure S12 and 13). On the other hand, the dyes with the same charge as the surface would be 55–60 Å away from the surface, indicating unfavorable adsorption. The MD simulation confirms that the polyelectrolyte-modified SERS substrate could selectively capture analytes with the opposite charge around its “hot spots” region, which could subsequently enhance their Raman signal.

Charge Transfer Studied with DFT Calculation. DFT calculation was performed for SY(−) on the FA-PDDA(+) system (Figure 6), and the results show that the adsorption of PDDA on Au surfaces is thermodynamically favorable as evidenced by its negative adsorption energy (−304.3 kcal mol^{-1}). Meanwhile, 0.28 electrons (e) were transferred from the Au cluster to PDDA molecules (Figure 6A), and the transferred electrons were aggregated at the $-\text{CH}_3$ group of PDDA, as the C atom served as the electron acceptor.⁴⁶

Figure 6. Electron transfer (A) from Au to PDDA(+) and (B) from SY(−) to FA-PDDA(+).

When a SY(−) molecule was introduced in the system (Figure 6B), its adsorption on FA-PDDA(+) surface was also favorable ($-124.7 \text{ kcal mol}^{-1}$). About 0.89 e were transferred from SY(−) to FA-PDDA(+), with an average of 0.15 e transferred from each $-\text{SO}_3$ group of SY(−) to the $-\text{CH}_3$ group of PDDA, and another 0.49 e were transferred to the Au surface (Figure S14). Similarly, for the SERS detection of MG(+) on FA-PSS(−), the CT mechanism may also play a role through the electron hopping effect (Figure S15).⁴⁷

To further justify the existence of CT mechanism, the SERS response of SY(−) on FA-PDDA(+) and MG(+) on FA-PSS(−) were compared with four excitation wavelengths at 478, 514, 633, and 785 nm (Figure S16). The peak intensity was selectively enhanced for SY(−) at 1551 cm^{-1} due to coupled $\delta(\text{C}-\text{C}-\text{R})$, $\rho(\text{N}-\text{H})$ and $\rho(\text{C}-\text{H})$ vibrations, and for MG(+) at 1595 cm^{-1} due to $\gamma(\text{C}-\text{C})_{\text{ring}}$ vibrations.^{44,48} In agreement with our DFT results, such a selective enhancement upon excitation by different laser lines implies the existence of CT mechanism.⁴⁹ This charge transfer was further confirmed by our fluorescence quenching experiments (Figure S17 and 18).

CONCLUSION

The 20 nm Au NPs were evenly deposited on magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2$ beads to fabricate a core–satellite FA hetero-nanostructure with tunable NP gap via the LBL encapsulation method. An average Au nanogap of 7 nm enables a substantial enhancement of the Raman signal. Further LBL decoration with a charged polyelectrolyte outside the satellite structure facilitates the selective adsorption and SERS detection of counter-charged food dye molecules. The high affinity and close contact facilitate charge transfer from food dye molecules to the SERS substrate. The significant Raman enhancement, the ease of the LBL fabrication, and the selective capture of analytes allow this multifunctional system to provide a new opportunity for rapid SERS detection of charged molecules in the field using a portable Raman spectrometer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b10230.

Experimental details for the fabrication of FA satellite structure, selective detection and adsorption experiments of functional FA for various food dyes, Mulliken charge and electron hopping between functional FA and food dyes, MD model setup, and DFT model setup (PDF) MD videos (ZIP)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the financial support of the National Basic Research Program of China (2015CB932003, 2014CB441102), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14020201), and the National Natural Science Foundation of China (41373123, 41425016).

REFERENCES

- (1) Zheng, Y. H.; Thai, T.; Reineck, P.; Qiu, L.; Guo, Y. M.; Bach, U. DNA-Directed Self-Assembly of Core-Satellite Plasmonic Nanostructures: A Highly Sensitive and Reproducible Near-IR SERS Sensor. *Adv. Funct. Mater.* **2013**, 23 (12), 1519–1526.
- (2) Zhang, H.; Cao, M. H.; Wu, W.; Xu, H. B.; Cheng, S.; Fan, L. J. Polyacrylonitrile/Noble Metal/ SiO_2 Nanofibers as Substrates for the Amplified Detection of Picomolar Amounts of Metal Ions through Plasmon-Enhanced Fluorescence. *Nanoscale* **2015**, 7 (4), 1374–1382.
- (3) Xie, W.; Walkenfort, B.; Schlucker, S. Label-Free SERS Monitoring of Chemical Reactions Catalyzed by Small Gold Nanoparticles Using 3D Plasmonic Superstructures. *J. Am. Chem. Soc.* **2013**, 135 (5), 1657–1660.
- (4) Gandra, N.; Abbas, A.; Tian, L. M.; Singamaneni, S. Plasmonic Planet-Satellite Analogues: Hierarchical Self-Assembly of Gold Nanostructures. *Nano Lett.* **2012**, 12 (5), 2645–2651.
- (5) Xiong, W.; Sikdar, D.; Yap, L. W.; Premaratne, M.; Li, X. Y.; Cheng, W. L. Multilayered Core-satellite Nanoassemblies with Fine-Tunable Broadband Plasmon Resonances. *Nanoscale* **2015**, 7 (8), 3445–3452.
- (6) Li, G. Z.; Liu, M.; Zhang, Z. Q.; Geng, C.; Wu, Z. B.; Zhao, X. Extraction of Methylmercury and Ethylmercury from Aqueous Solution Using Surface Sulfhydryl-Functionalized Magnetic Mesoporous Silica Nanoparticles. *J. Colloid Interface Sci.* **2014**, 424, 124–131.
- (7) Wu, Y. P.; Li, P.; Yang, L. B.; Liu, J. H. Individual SERS Substrate with Core-Satellite Structure Decorated in Shrinkable Hydrogel Template for Pesticide Detection. *J. Raman Spectrosc.* **2014**, 45 (1), 68–74.
- (8) Liu, H. L.; Yang, Z. L.; Meng, L. Y.; Sun, Y. D.; Wang, J.; Yang, L. B.; Liu, J. H.; Tian, Z. Q. Three-Dimensional and Time-Ordered Surface-Enhanced Raman Scattering Hotspot Matrix. *J. Am. Chem. Soc.* **2014**, 136 (14), 5332–5341.
- (9) Dey, P.; Zhu, S. L.; Thurecht, K. J.; Fredericks, P. M.; Blakey, I. Self Assembly of Plasmonic Core-Satellite Nano-Assemblies Mediated by Hyperbranched Polymer Linkers. *J. Mater. Chem. B* **2014**, 2 (19), 2827–2837.
- (10) Yang, L. B.; Li, P.; Liu, J. H. Progress in Multifunctional Surface-Enhanced Raman Scattering Substrate for Detection. *RSC Adv.* **2014**, 4 (91), 49635–49646.
- (11) Dui, J. N.; Zhu, G. Y.; Zhou, S. M. Facile and Economical Synthesis of Large Hollow Ferrites and Their Applications in Adsorption for As(V) and Cr(VI). *ACS Appl. Mater. Interfaces* **2013**, 5 (20), 10081–10089.
- (12) Liu, Y. B.; Wang, Y. Q.; Zhou, S. M.; Lou, S. Y.; Lin, Y.; Gao, T.; Wu, X. P.; Shi, X. J.; Wang, K. Synthesis of High Saturation Magnetization Superparamagnetic Fe_3O_4 Hollow Microspheres for Swift Chromium Removal. *ACS Appl. Mater. Interfaces* **2012**, 4 (9), 4913–4920.
- (13) Baik, S. Y.; Cho, Y. J.; Lim, Y. R.; Im, H. S.; Jang, D. M.; Myung, Y.; Park, J.; Kang, H. S. Charge-Selective Surface-Enhanced Raman Scattering Using Silver and Gold Nanoparticles Deposited on Silicon-Carbon Core-Shell Nanowires. *ACS Nano* **2012**, 6 (3), 2459–2470.

- (14) Panarin, A. Y.; Terekhov, S. N.; Kholostov, K. I.; Bondarenko, V. P. SERS-Active Substrates Based on N-Type Porous Silicon. *Appl. Surf. Sci.* **2010**, 256 (23), 6969–6976.
- (15) Tian, L. M.; Tadepalli, S.; Farrell, M. E.; Liu, K. K.; Gandra, N.; Pellegrino, P. M.; Singamaneni, S. Multiplexed Charge-Selective Surface Enhanced Raman Scattering Based on Plasmonic Calligraphy. *J. Mater. Chem. C* **2014**, 2 (27), 5438–5446.
- (16) Zhu, Y. Q.; Zhang, L.; Yang, L. B. Designing of the Functional Paper-Based Surface-Enhanced Raman Spectroscopy Substrates for Colorants Detection. *Mater. Res. Bull.* **2015**, 63, 199–204.
- (17) Srivastava, S.; Nykypanchuk, D.; Fukuto, M.; Gang, O. Tunable Nanoparticle Arrays at Charged Interfaces. *ACS Nano* **2014**, 8 (10), 9857–9866.
- (18) Jiang, S. H.; Xu, J. F.; Xu, P. D.; Liu, L. J.; Chen, Y.; Qiao, C. S.; Yang, S. F.; Sha, Z. L.; Zhang, J. K. A Novel Molecularly Imprinted Sensor for Direct Tartrazine Detection. *Anal. Lett.* **2014**, 47 (2), 323–330.
- (19) Van Rijn, P.; Tutus, M.; Kathrein, C.; Mougin, N. C.; Park, H.; Hein, C.; Schurings, M. P.; Boker, A. Ultra-Thin Self-Assembled Protein-Polymer Membranes: A New Pore Forming Strategy. *Adv. Funct. Mater.* **2014**, 24 (43), 6762–6770.
- (20) Lee, S. K.; Tung, C. H. A Fabricated siRNA Nanoparticle for Ultralong Gene Silencing in Vivo. *Adv. Funct. Mater.* **2013**, 23 (28), 3488–3493.
- (21) Zhang, K.; Luo, P.; Wu, J.; Wang, W.; Ye, B. Highly Sensitive Determination of Sunset Yellow in Drink Using a Poly (L-Cysteine) Modified Glassy Carbon Electrode. *Anal. Methods* **2013**, 5 (19), 5044–5050.
- (22) Zhu, Y. Q.; Zhang, L.; Yang, L. B. Designing of the Functional Paper-Based Surface-Enhanced Raman Spectroscopy Substrates for Colorants Detection. *Mater. Res. Bull.* **2015**, 63, 199–204.
- (23) Du, J. J.; Jing, C. Y. Preparation of Thiol Modified Fe_3O_4 @Ag Magnetic SERS Probe for PAHs Detection and Identification. *J. Phys. Chem. C* **2011**, 115 (36), 17829–17835.
- (24) Du, J. J.; Cui, J. L.; Jing, C. Y. Rapid in Situ Identification of Arsenic Species Using a Portable Fe_3O_4 @Ag SERS Sensor. *Chem. Commun.* **2014**, 50 (3), 347–349.
- (25) Xu, J. W.; Du, J. J.; Jing, C. Y.; Zhang, Y. L.; Cui, J. L. Facile Detection of Polycyclic Aromatic Hydrocarbons by a Surface-Enhanced Raman Scattering Sensor Based on the Au Coffee Ring Effect. *ACS Appl. Mater. Interfaces* **2014**, 6 (9), 6891–6897.
- (26) Deng, Y. H.; Qi, D. W.; Deng, C. H.; Zhang, X. M.; Zhao, D. Y. Superparamagnetic High-Magnetization Microspheres with an Fe_3O_4 @ SiO_2 Core and Perpendicularly Aligned Mesoporous SiO_2 Shell for Removal of Microcystins. *J. Am. Chem. Soc.* **2008**, 130 (1), 28–29.
- (27) Stöber, W.; Fink, A.; Bohn, E. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *J. Colloid Interface Sci.* **1968**, 26 (1), 62–69.
- (28) Ge, X. X.; Tao, Y.; Zhang, A. D.; Lin, Y. H.; Du, D. Electrochemical Detection of Dual Exposure Biomarkers of Organophosphorus Agents Based on Reactivation of Inhibited Cholinesterase. *Anal. Chem.* **2013**, 85 (20), 9686–9691.
- (29) Bai, Y. H.; Li, J. Y.; Xu, J. J.; Chen, H. Y. Ultrasensitive Electrochemical Detection of DNA Hybridization Using Au/ Fe_3O_4 Magnetic Composites Combined with Silver Enhancement. *Analyst* **2010**, 135 (7), 1672–1679.
- (30) Daneshvar, N.; Khataee, A.; Rasoulifard, M.; Pourhassan, M. Biodegradation of Dye Solution Containing Malachite Green: Optimization of Effective Parameters Using Taguchi Method. *J. Hazard. Mater.* **2007**, 143 (1), 214–219.
- (31) Alves, S. P.; Brum, D. M.; Branco de Andrade, É. C.; Pereira Netto, A. D. Determination of Synthetic Dyes in Selected Foodstuffs by High Performance Liquid Chromatography with UV-DAD Detection. *Food Chem.* **2008**, 107 (1), 489–496.
- (32) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. Uff, A Full Periodic-Table Force-Field for Molecular Mechanics and Molecular-Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, 114 (25), 10024–10035.
- (33) Zhao, T.; Xu, G.; Yuan, S.; Chen, Y.; Yan, H. Molecular Dynamics Study of Alkyl Benzene Sulfonate at Air/Water Interface: Effect of Inorganic Salts. *J. Phys. Chem. B* **2010**, 114 (15), 5025–5033.
- (34) Verlet, L. Computer “Experiments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.* **1967**, 159 (1), 98–103.
- (35) He, G.; Pan, G.; Zhang, M. Assembling Structures and Dynamics Properties of Perfluorooctane Sulfonate (PFOS) at Water-Titanium Oxide Interfaces. *J. Colloid Interface Sci.* **2013**, 405, 189–194.
- (36) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, 117 (1), 1–19.
- (37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865–3868.
- (38) Li, J. F.; Huang, Y. F.; Ding, Y.; Yang, Z. L.; Li, S. B.; Zhou, X. S.; Fan, F. R.; Zhang, W.; Zhou, Z. Y.; Wu, D. Y.; Ren, B.; Wang, Z. L.; Tian, Z. Q. Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy. *Nature* **2010**, 464 (7287), 392–395.
- (39) Klinkova, A.; Therien-Aubin, H.; Ahmed, A.; Nykypanchuk, D.; Choueiri, R. M.; Gagnon, B.; Muntyanu, A.; Gang, O.; Walker, G. C.; Kumacheva, E. Structural and Optical Properties of Self-Assembled Chains of Plasmonic Nanocubes. *Nano Lett.* **2014**, 14 (11), 6314–6321.
- (40) Liu, X.; Lebedkin, S.; Besser, H.; Pfleging, W.; Prinz, S.; Wissmann, M.; Schwab, P. M.; Nazarenko, I.; Guttman, M.; Kappes, M. M.; Lemmer, U. Tailored Surface-Enhanced Raman Nanopillar Arrays Fabricated by Laser-Assisted Replication for Biomolecular Detection Using Organic Semiconductor Lasers. *ACS Nano* **2015**, 9 (1), 260–270.
- (41) Huck, C.; Neubrech, F.; Vogt, J.; Toma, A.; Gerbert, D.; Katzmann, J.; Hartling, T.; Pucci, A. Surface-Enhanced Infrared Spectroscopy Using Nanometer-Sized Gaps. *ACS Nano* **2014**, 8 (5), 4908–4914.
- (42) Cheng, L.; Ma, C. S.; Yang, G.; You, H. J.; Fang, J. X. Hierarchical Silver Mesoparticles with Tunable Surface Topographies for Highly Sensitive Surface-Enhanced Raman Spectroscopy. *J. Mater. Chem. A* **2014**, 2 (13), 4534–4542.
- (43) Lee, J. H.; You, M. H.; Kim, G. H.; Nam, J. M. Plasmonic Nanosnowmen with a Conductive Junction as Highly Tunable Nanoantenna Structures and Sensitive, Quantitative and Multiplexable Surface-Enhanced Raman Scattering Probes. *Nano Lett.* **2014**, 14 (11), 6217–6225.
- (44) Xie, Y. F.; Chen, T.; Cheng, Y. L.; Wang, H. Y.; Qian, H.; Yao, W. R. SiO_2 @Au Nanoshells-Based SERS Method for Detection of Sunset Yellow and Chrysoidine. *Spectrochim. Acta, Part A* **2014**, 132, 355–360.
- (45) Peyratout, C.; Donath, E.; Daehne, L. Electrostatic Interactions of Cationic Dyes with Negatively Charged Polyelectrolytes in Aqueous Solution. *J. Photochem. Photobiol., A* **2001**, 142 (1), 51–57.
- (46) Kuznetsov, M. L.; Kukushkin, V. Y. Theoretical Study of Reactant Activation in 1,3-dipolar Cycloadditions of Cyclic Nitrones to Free and Pt-Bound Nitriles. *J. Org. Chem.* **2006**, 71 (2), 582–592.
- (47) Schlenoff, J. B.; Laurent, D.; Ly, H.; Stepp, J. Redox-Active Polyelectrolyte Multilayers. *Chem. Eng. Technol.* **1998**, 21 (9), 757–759.
- (48) Xiao, G. N.; Man, S. Q. The Effect of L-Cysteine on Surface-Enhanced Raman Scattering of Malachite Green in Silver Colloids. *Spectrosc. Lett.* **2013**, 46 (8), 577–582.
- (49) Mao, Z.; Song, W.; Xue, X.; Ji, W.; Chen, L.; Lombardi, J. R.; Zhao, B. Multiphonon Resonant Raman Scattering and Photoinduced Charge-Transfer Effects at ZnO-Molecule Interfaces. *J. Phys. Chem. C* **2012**, 116 (51), 26908–26918.