Fabrication of Poly(styrene-co-maleic anhydride)@Ag Spheres with High Surface Charge Intensity and their Self-Assembly into Photonic Crystal Films

Jiajie Bi, Genrui Fan, Suli Wu,* Xin Su, Hongbo Xia, and Shu-Fen Zhang

Herein, we developed a method to prepare monodisperse poly(styrene-co-maleic anhydride)@Ag (PSMA@Ag) core–shell microspheres with high surface charge intensity by using in situ reduction methods. In this method, ethylenediamine tetraacetate sodium salt (Na₂EDTA) was used as a reducing agent to promote the growth of Ag, and at the same time endowed the PSMA@Ag spheres with a surface charge. The monodispersity of PSMA and PSMA@Ag and the ordered array of the photonic crystal films were characterized by using SEM. The formation of Ag nanoparticles was confirmed by using TEM, HR-TEM, and XRD characterizations. Due to the existence of surface charges, the obtained PSMA@Ag microspheres easily self-assembled to form photonic crystal structures. In addition, the surface-enhanced Raman scattering (SERS) activity of the PSMA@Ag photonic crystal films was evaluated by detecting the signal from Raman probe molecules, 4-aminothiophenol (4-ATP). The PSMA@Ag photonic crystal films exhibited a high SERS effect, a low detection limit of up to 10⁻⁸ for 4-ATP, good uniformity, and reproducibility.

1. Introduction

In recent years, three-dimensional (3D) metallic (Au and Ag) photonic crystals (PCs) have received extensive attention due to the special features of PCs (large surface area and ability to modulate light) and the plasmonic enhancement effect of noble metals. They have promising potential applications in many fields, such as plasmonic enhanced emission[1] and surface-enhanced Raman scattering (SERS).[2] 3D metal–dielectric PC structures have many advantages. First, the distribution of metal nanoparticles is relatively uniform within the PC films, which is beneficial to obtain uniform and reproducible signals. Furthermore, the high density of electromagnetic modes at the band edge of the photonic bandgap may lead to a strong light–matter interaction. To date, most of the preparation strategies for 3D metallic PCs have focused on the deposition of noble metals on pre-prepared inverse-opal or opal PCs.[3] Although the fabrication of noble-metal-decorated PC films by the self-assembly of metal-decorated dielectric spheres will guarantee the uniform dispersion of metals within the PCs, there are few reports on the fabrication of opal PCs by the self-assembly of noble-metal-decorated dielectric spheres because these decorated spheres are difficult to self-assemble due to their high density and low surface charge intensity.

A core–shell strategy is the commonly used method to fabricate metallic–dielectric composite nanoparticles. Many efforts have been devoted to core–shell composite spheres with a dielectric solid sphere (e.g., silica, polystyrene) surrounded by a Au or Ag metallic nanoshell owing to their wide applications in catalysis,[4] optoelectronics, PCs,[5] sensing,[6] chemical separation and detection,[7] plasmonics, and SERS.[8] Various preparation methods have been developed, such as thermal evaporation, magnetron sputtering, ultrasound irradiation,[9] electroless deposition,[10] self-assembly,[11] solvent-assisted deposition,[a] and in situ reduction methods.[4a, 12] Of these methods, the in situ reduction method is simple to operate and can easily introduce surface-modifying groups.

Herein, we developed a modified in situ reduction method to prepare poly(styrene-co-maleic anhydride)@Ag (PSMA@Ag) core–shell microspheres with high surface charge intensity. As illustrated in Scheme 1, monodisperse PSMA spheres prepared by emulsion polymerization were first modified with polyethyleneimine (PEI). Subsequently, Ag seeds were formed in situ

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[a] J. J. Bi, G. R. Fan, Prof. Dr. S. L. Wu, Dr. X. Su, H. B. Xia, Prof. Dr. S.-F. Zhang
State Key Laboratory of Fine Chemicals
Dalian University of Technology
Dalian, 116024 (P. R. China)
E-mail: wusuli@dlut.edu.cn

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Scheme 1. Schematic illustration of the preparation of PSMA@Ag core–shell microspheres and their self-assembly; PEI = polyethyleneimine.
and immobilized on the surface of the PEI-modified colloidal PSMA spheres by addition of a solution of AgNO₃. Then, ethylenediamine tetraacetic acid tetrasodium salt (Na₂EDTA) was added to the dispersion to promote the growth of Ag seeds, increase the thickness of the Ag shell, and, importantly, to endow the particle with a surface charge (carboxyl and amine groups), which facilitated the self-assembly of the core–shell structures. Finally, PSMA@Ag PC films were prepared by assembly of the PSMA@Ag core–shell microspheres. The SERS activity of the PSMA@Ag PC films was then evaluated by detecting the signal from a Raman probe molecule, 4-aminothiophenol (4-ATP). The obtained substrates showed a remarkable SERS activity and Raman signal reproducibility.

2. Results and Discussion

The monodisperse PSMA spheres were prepared by using emulsion polymerization method as described in the Experimental Section. By controlling the amount of emulsifier, monodisperse PSMA spheres with diameters of 180, 210, and 240 nm were obtained. The SEM images in Figure S1 in the Supporting Information show that the PSMA spheres have highly uniform sizes and a smooth surface. In particular, they have a tendency to self-assemble into ordered structures. To investigate the surface charges of the prepared PSMA spheres, the zeta potentials of the PSMA colloidal microspheres with different diameters were measured and are summarized in Table S1. The zeta potentials of these colloidal microspheres were about −43 to −46 mV, which indicated the existence of carboxyl groups on the surface of the PSMA spheres that, therefore, resulted in their good dispersity in water.

By using the obtained PSMA spheres as a core, PSMA@Ag core–shell microspheres were prepared by an in situ reduction method. The fabrication procedure is shown schematically in Scheme 1. In the first step, monodisperse PSMA spheres were modified with PEI, which can complex with Ag⁺ and reduce Ag⁺ to Ag when heated. The zeta potentials of the PEI-modified PSMA colloidal microspheres with different diameters were also measured and are summarized in Table S2. Compared with the PSMA microspheres, the zeta potentials of PSMA@PEI colloidal microspheres changed from −43 to −46 mV to 11.5 to 15.1 mV. A solution of AgNO₃ was then added to the PEI-modified PSMA colloidal and Ag seeds were formed in situ and immobilized on the surface of PSMA by heating. Finally, ethylenediamine tetraacetic acid tetrasodium salt (Na₂EDTA) was added to the dispersion to promote the growth of Ag seeds, increase the thickness of the Ag shell, and provide the particle with enough surface charges.

During the core–shell microspheres formation process, the experimental parameters, such as the reaction temperature, the concentration of the solution of AgNO₃, and the concentration of Na₂EDTA solution were optimized for the improvement of Ag coverage. The optimum parameters were obtained through a series of experiments, and well-dispersed and uniformly coated PSMA@Ag core–shell microspheres with diameters of 190, 225, and 250 nm were successfully fabricated. The SEM images in Figure 1a–c clearly indicate that the resultant PSMA@Ag core–shell microspheres were monodisperse, with Ag nanoparticles uniformly coated on their surfaces. Figure 1d shows the TEM image of a PSMA@Ag core–shell microsphere (diameter 250 nm), and further confirms the formation of Ag nanoparticles on the surface of the PSMA spheres. The corresponding HR-TEM image (Figure 1e) shows the crystalline quality and the size (≈10 nm) of the Ag nanoparticles. The observed lattice fringe spacing of 0.23 nm corresponds to the (1 1 1) lattice plane of cubic-phase Ag (JCPDS 04-0783). These results reveal that monodisperse PSMA@Ag core–shell microspheres with Ag nanoparticles uniformly coated on the surfaces were prepared.

To investigate the surface properties of PSMA@Ag core–shell microspheres, FTIR and zeta-potential measurements were performed. The FTIR spectra of the PSMA microspheres with and without Ag are presented in Figure S2. Compared with the results for PSMA, the absorption peaks at about 1383 and 1700 cm⁻¹ in the IR spectra of PSMA@Ag microspheres should be ascribed to NH₂,¹⁰ which means the PSMA@Ag spheres have positive surface charges. In light of this, these PSMA@Ag spheres exhibit high surface charge intensity with a zeta potential of 28.8 to 32.4 mV (as shown in Table S3), which is obviously higher than that of PSMA@PEI. This high surface charge intensity is beneficial for the self-assembly of these spheres into PCs with a long-range ordered structure.

To acquire structural information, the samples were further characterized by using XRD, and the results are present in Figure 1f. The XRD patterns of the PSMA@Ag core–shell microspheres revealed diffraction peaks centered at 38.1, 44.3, 64.4, and 77.5°, which were identified as diffraction peaks from the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) faces of metallic Ag, respectively.

Due to the high charge intensity on the surface of the PSMA@Ag spheres, the as-prepared PSMA@Ag colloidal microspheres can self-assemble into close-packed PC structures through a simple vertical-deposition process. PSMA@Ag core–shell microspheres with diameters of 190, 225, and 250 nm were used to fabricate PC films. The SEM images of the surface and cross-section of the PC films (Figure 2a–f) confirmed that...
the PSMA@Ag microspheres can self-assemble into an ordered PC structure.

Next, the optical properties of the obtained PC films were investigated. The reflectance spectra (Figure 2g–i) of PC films fabricated from PSMA@Ag spheres with different diameters were measured at normal incidence to detect the photonic bandgap (PBG). The PBG effects and Bragg diffraction arise from the periodicity of the PSMA@Ag PC films, which give rise to the reflection peaks. The peak positions of PSMA@Ag PC films with different diameters of PSMA@Ag (190, 225, and 250 nm) were \(\lambda = 467, 552, \) and 620 nm, respectively, and these films displayed the corresponding structure colors, as shown in the insets of Figure 2g–i.

Due to the existence of a PBG, the PCs can be used to modulate localized electric fields effectively, and it is expected that through a combination of the effects of plasma resonance and PBG, the Raman scattering signals can be enhanced more significantly. To evaluate the SERS effect of the PSMA@Ag PC films, 4-aminothiophenol (4-ATP) with a concentration of \(10^{-6} \text{ mol L}^{-1}\) was selected as a Raman probe. The Raman spectra of the three prepared PC films (PBGs at \(\lambda = 467, 552, \) and 620 nm) after absorption of 4-ATP (\(10^{-6} \text{ mol L}^{-1}\)) at room temperature and then dried in air, and their Raman measurement results are illustrated in Figure 3b. The results showed that as the Ag content increased, larger SERS intensities were obtained owing to a greater number of hot spots. In a control experiment, a PSMA@Ag film with a disordered structure, a pure Ag film, and a PC film were used as substrates for SERS. As indicated in Figure S3, only the substrates prepared with an ordered PSMA@Ag PC film possessed the strongest SERS enhancement effect.

To prove the excellent SERS ability of the PSMA@Ag PC films further, SERS spectra were collected for 250 nm PSMA@Ag PC films with different concentrations of 4-ATP. As shown in Figure 4a, the Raman characteristic bands of 4-ATP were still clearly detected even when the 4-ATP concentration was reduced to \(10^{-8} \text{ mol L}^{-1}\). The low SERS detection limit of the PSMA@Ag PC film substrate may be attributed to both the unique structures with a high density of hot spots and high surface area. In addition to the high sensitivity, Figure 4b shows the Raman spectra recorded at five random spots on the substrate, which demonstrated the good uniformity of the substrate because the relative standard deviation (RSD) of the band intensity of 4-ATP is less than 15%.

In addition, the reproducibility of substrate was evaluated by measuring the same PSMA@Ag film five times, and the results show the good reproducibility of the PC film (Figure S4).
The stability of substrates was evaluated by measuring the change in the SERS effect for substrates stored for 1, 10, 20, 30, and 60 d. Before measurement, the substrates were immersed in a solution of 4-ATP (10⁻⁶ M) for 12 h, then the Raman spectra was recorded under λ = 532 nm laser excitation. As shown in Figure S5, after 30 d the SERS effect of the substrates decreased slightly and strong SERS signals were still observed. This suggests that the PSMA@Ag PC films have good stability.

3. Conclusions

In summary, PSMA@Ag core–shell microspheres with surface charges were prepared by an in situ reduction method with Na₂EDTA as reducing agent. Monodisperse PSMA@Ag core–shell microspheres with Ag nanoparticles uniformly coated on their surface were obtained. It should be highlight that the PSMA@Ag core–shell microspheres exhibited high surface charge intensity, with a zeta potential of 28.8 to 32.4 mV. The PSMA@Ag PC films were prepared by self-assembly of the PSMA@Ag core–shell microspheres by a vertical-deposition method. The PSMA@Ag PC film, as a SERS substrate, exhibited high SERS enhancement. The content of Ag nanoparticles and position of the PBG of the substrate are key factors that determine the SERS effect. A detection limit of 10⁻⁸ m was achieved for 4-ATP. The relative deviation in the band intensity of five random spots on the substrate was less than 15 %, which demonstrated the good uniformity and reproducibility of the substrate.

Experimental Section

Materials

Styrene (St), maleic anhydride (MA), lauryl sodium sulfate (SDS), potassium persulfate, silver nitrate, ethylenediamine tetraacetic acid tetrasodium salt (Na₂EDTA), ethyl alcohol, concentrated sulfuric acid, and 4-ATP were purchased from Sinopharm Chemical Reagent Co. All chemicals were used without further purification except styrene, which was purified by distillation under reduced pressure.

Preparation of PSMA Microspheres

PSMA microspheres were prepared by the emulsifier-free emulsion copolymerization of St and MA. SDS (0.024 g) was dissolved in deionized water (50 mL), then the reaction mixture was heated to 80 °C and purged with nitrogen for 20 min with constant stirring (300 min⁻¹) in a three-necked round-bottomed flask equipped with a condenser and an inlet for nitrogen. Then, styrene (3 g) was added just prior to initiation. Initiation was performed by using potassium persulfate (0.05 g). MA (0.8 g) was added after 1 h, then the reaction mixture was vigorously stirred at 80 °C for 4 h under a nitrogen atmosphere. The precipitants were collected by centrifuging the mixture at 10 000 rpm for 25 min and then washing with water. A solution of AgNO₃ (5 mL, 10 g L⁻¹) was mixed with the dispersion of PEI-modified PSMA colloids, then the mixture was heated to 80 °C and held at this temperature for 2 h. At this temperature, a solution of Na₂EDTA (5 mL, 5 g L⁻¹) was added dropwise with stirring. The obtained composite was collected by centrifugation and washed with deionized water.

Self-Assembly of PSMA@Ag Microspheres

Microscope slides were cut into ≈ 1.0 × 1.0 cm pieces and soaked in concentrated sulfuric acid with ultrasonication for 30 min, then rinsed with deionized water. The slides were then used as substrates for the self-assembly of PSMA@Ag microspheres. The PSMA@Ag PC films were prepared by self-assembly of PSMA@Ag core–shell microspheres in a vertical-deposition process. Each cleaned substrate was dipped vertically into a suspension of PSMA@Ag in a vial. The suspensions were placed in a vacuum oven at 50 °C until the water had completely evaporated from the dispersion. The colloidal crystals were then allowed to dry naturally at RT for 12 h.

Characterization and Raman Spectroscopy Measurements

The morphologies of PSMA spheres, PMSA@Ag core–shell microspheres, and the PC films were characterized by using a Nova Nanosem 450 field-emission scanning electron microscope and a Tecnai G220 S-Twin microscope transmission electron microscope. Powder X-ray diffraction (XRD) patterns were measured by using a Rigaku D/MAX-2400 diffractometer with CuKα radiation. A zeta-potential analyzer (Zetasizer 1000, Malvern, UK) was used to measure the zeta potential of the PSMA and PSMA@Ag colloids. The reflection spectra of the films were measured by using a Hitachi U-4100 spectrophotometer. The incidence and reflection angles were always kept the same during the measurements.

Raman microprobe measurements were performed by using a DRX laser confocal micro Raman spectrometer. The spectra measured on the samples were obtained by using an Ar⁺ laser (λ = 514 nm) with 5 mW laser power as the excitation source. The spectra were collected with an average spot diameter of 1 μm. 4-ATP was used as the reporter probe for the SERS measurements. The as-prepared substrates were immersed in aqueous 4-ATP of different concentrations for 12 h, then removed and dried in the dark for SERS detection.

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Conflict of Interest

The authors declare no conflict of interest.
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[1] a) W. Niu, L. T. Su, R. Chen, H. Chen, Y. Wang, A. Palaniappan, H. Sun, A. I. Tok, Nanoscale 2014, 6, 817–824; b) Z. Yin, H. Li, W. Xu, S. Cui, D. Zhou, X. Chen, Y. Zhu, G. Qin, H. Song, Adv. Mater. 2016, 28, 2518–2525; c) J. Yang, Z. Yang, Y. Wang, J. Qiu, Z. Song, J. Non-Cryst. Solids 2016, 437, 53–57; d) B. Shao, Z. Yang, Y. Wang, J. Li, J. Yang, J. Qiu, Z. Song, ACS Appl. Mater. Interfaces 2015, 7, 25211–25218; e) J. Liao, Z. Yang, S. Lai, B. Shao, J. Li, J. Qiu, Z. Song, Y. Yang, J. Phys. Chem. C 2014, 118, 17992–17999.

[2] a) C. Y. Wu, C. C. Huang, J. S. Jhang, A. C. Liu, C.-C. Chiang, M.-L. Hsieh, P.-J. Huang, L. D. Tuyen, L. Q. Minh, T. S. Yang, L.-K. Chau, H.-C. Kan, C. C. Hsu, Opt. Express 2009, 17, 21522–21529; b) S. Kubo, Z. Gu, D. A. Tryk, Y. Ohko, O. Sato, A. Fujishima, Langmuir 2002, 18, 5043–5046; c) Y. Zhao, X. J. Zhang, J. Ye, M. Chen, S. P. Lai, W. J. Zhang, S. T. Lee, ACS Nano 2011, 5, 3027–3033.

[3] a) Z. Chen, L. Fang, W. Dong, F. Zheng, M. Shen, J. Wang, J. Mater. Chem. A 2014, 2, 824–832; b) L. D. Tuyen, A. C. Liu, C.-C. Huang, P.-C. Tsai, J. H. Lin, C.-W. Wu, L.-K. Chau, T. S. Yang, L. Q. Minh, H.-C. Kan, C. C. Hsu, Opt. Express 2012, 20, 29266–29275; c) X. Zhao, J. Xue, Z. Mu, Y. Huang, M. Lu, Z. Gu, Biosens. Bioelectron. 2015, 72, 268–274; d) L. Lu, I. Randjelovic, R. Capek, N. Gaponik, J. Yang, H. Zhang, A. Eychmüller, Chem. Mater. 2005, 17, 5731–5736.

[4] a) S. Jana, S. K. Ghosh, S. Nath, S. Pande, S. Prabha, S. Panigrahi, S. Basu, T. Endo, T. Pal, Appl. Catal. A 2006, 313, 41–48; b) F. Pang, Y. Jiang, Y. Zhang, M. He, J. Ge, J. Mater. Chem. A 2015, 3, 21439–21443.

[5] a) J. Zhang, J. Liu, S. Wang, P. Zhan, Z. Wang, N. Ming, Adv. Funct. Mater. 2004, 14, 1089–1096; b) W. Zhu, Y. Wu, C. Wang, M. Zhang, G. Dong, Nano-Micro Lett. 2013, 5, 182–190.

[6] a) Y. Zhang, Q. Fu, J. Ge, Nat. Commun. 2015, 6, 7510–7517; b) Y. Zhang, Q. Fu, J. Ge, Small 2017, 13, 1603351.

[7] a) Q. Fu, B. Zhu, J. Ge, Nanoscale 2017, 9, 2457–2463.

[8] a) S. Long, L. Li, H. Guo, W. Yang, F. Lu, Dyes Pigments 2012, 95, 473–477.

[9] a) Y. Ma, Q. Zhang, Appl. Surf. Sci. 2012, 258, 7774–7780; b) Y. Kobayashi, V. Salgueirinho-Macedo, L. M. Liz-Marzán, Chem. Mater. 2001, 13, 1630–1633.

[10] a) T. Ji, V. G. Lirtsman, Y. Avnir, D. Davidov, Adv. Mater. 2001, 13, 1253–1256.

[11] a) C. Zhang, X. Zhu, H. Li, I. Khan, M. Imran, L. Wang, J. Bao, X. Cheng, Nanoscale Res. Lett. 2012, 7, 580; b) Z. Chen, C. Xin, L. Zheng, G. Tian, T. Cui, Z. Kai, Y. Bai, J. Colloid Interface Sci. 2005, 285, 146–151.

[12] a) W. Van, F. T. J. Dunai, R. T. Van Balen, W. Klas, A. L. M. Verbers, S. Passchier, U. Herpers, J. Ryczkowski, Vib. Spectrosc. 2000, 22, 55–62.

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