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Highly Sensitive Surface-Enhanced Raman Spectroscopy (SERS) Platforms Based on Silver Nanostructures Fabricated on Polyaniline Membrane Surfaces

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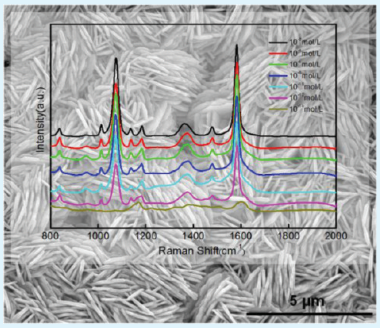
S Supporting Information

ABSTRACT: Here, we demonstrate a facile synthesis of homogeneous Ag nanostructures fully covering the polyaniline (PANI) membrane surface simply by introducing organic acid in the $AgNO_3$ reaction solution, as an improved technique to fabricate well-defined Ag nanostructures on PANI substrates through a direct chemical deposition method [*Langmuir* **2010**, *26*, 8882]. It is found that the chemical nature of the acid is crucial to create a homogeneous nucleation environment for Ag growth, where, in this case, homogeneous Ag nanostructures that are assembled by Ag nanosheets are produced with the assistance of succinic acid and lactic acid, but only scattered Ag particles with camphorsulfonic acid. Improved surface wettability of PANI membranes after acid doping may also account for the higher surface coverage of Ag nanostructures. The Ag nanostructures fully covering the PANI surface are extremely sensitive in the detection of a target analyte, 4-mercaptobenzoic acid (4-MBA), using surface-enhanced Raman spectroscopy (SERS), with a detection limit of 10^{-12} M. We believe the facilely fabricated SERS-active substrates based on conducting polymer-mediated growth of Ag nanostructures can be promising in the trace detection of chemical and biological molecules.



KEYWORDS: *surface-enhanced Raman spectroscopy, silver, polyaniline, membrane, nanostructure*

I. INTRODUCTION

Surface-enhanced Raman spectroscopy (SERS), applying the greatly enhanced electromagnetic field as well as the localized surface plasmon resonances generated at the metal surfaces upon incident laser, has been recognized as a powerful probe for trace detection of chemical and biological molecules, since the availability of single molecule detection.[1−3] Because SERS "hot spots" usually reside in the interstitial voids of metal nanoparticles and metal structures with intersections, bifurcations, and high radius of curvatures, exquisite preparation of metal nanoparticles with controlled size and morphology and delicate manipulation of the nanoparticle assemblies are required in order to maximize the sensitivity of the prepared SERS platforms. To this objective, various designs of SERS-active substrates have been reported, such as roughened metal substrates,[4−6] metal nanoparticle assemblies,[7−11] porous or holey substrates,[12−14] and even semiconductor-based substrates.[15−18] However, SERS substrates must be reproducible, highly sensitive, facile for fabrication, and have site-independent "hot spots", while most of the above-mentioned candidates require relatively complicated and expensive manipulations.

In our recent works, we have demonstrated that, on polyaniline (PANI) substrates, metals such as Ag, Au, Pt, and Pd can be spontaneously grown on the PANI surfaces through a direct chemical deposition technique, where the size and morphology of the metal structures can be manipulated by the chemical nature and surface chemistry of PANI, and reaction conditions such as temperature, metal salt concentration, reaction time, etc.[19−27] Particularly, Ag nanostructures fabricated on the PANI surface show highly sensitive response in SERS detection.[21−24] However, the addition of conductive additives to the PANI substrate or prefabrication of a Au nanolayer on the PANI surface is required to obtain homogeneous Ag nanostructures fully covered the substrate.[22,23] Recently, we come to realize that the addition of a very small amount of organic acid to $AgNO_3$ solution can lead to homogeneous Ag nanostructures that are inaccessible in just $AgNO_3$ solution.

In this paper, we demonstrate an improved yet facile technique to fabricate well-defined Ag nanostructures fully covering the PANI membranes, where conductive additives and prefabricated Au nanolayer are not required. The as-prepared Ag nanostructures show extremely high sensitivity (up to 10^{-12} M) in SERS detection of a target analyte, 4-mercaptobenzoic

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acid (4-MBA). We believe this facile fabrication of Ag nanostructures on PANI surfaces can be promising in chemical and biological detection, based on SERS techniques.

II. EXPERIMENTAL SECTION

Materials. PANI emeraldine base (EB) powder (Aldrich), *N*-methyl-2-pyrrolidone (NMP, 99% Aldrich), heptamethyl-enimine (HPMI, 98% Acros), $AgNO_3$ (99.9999% Aldrich), *R*-(−)-camphorsulfonic acid (98% Aldrich), lactic acid (Acros), succinic acid (>99.5% Fisher), and 4-mercaptobenzoic acid (4-MBA, Aldrich 90%) were used as received.

Fabrication of PANI Membranes. PANI membranes are fabricated by a phase inversion method using water as the coagulation bath.[22,26] In a typical experiment, 1.15 g of PANI (EB) powder, 4.14 g of NMP, and 0.747 g of HPMI were mixed in a 12-mL Teflon vial. The mixture was stirred for 0.5−1 h to form a homogeneous solution, followed by being poured onto a glass substrate and spread into a wet film using a gardener's blade with a controlled thickness. The wet film was then immersed into a water bath and kept in the water bath for at least 24 h. The resulting membrane was then dried at room temperature for 6 h, and then cut into 5 mm × 5 mm pieces. A part of the PANI pieces was doped in 0.25 M *R*-(−)-camphorsulfonic acid for 3 days before being used for Ag growth, and others remain undoped.

Growth of Ag Nanostructures on PANI Membranes. The growth of Ag nanostructures on a PANI surface was conducted as follows: one piece of undoped or doped PANI membrane was immersed in a mixture solution of 1 mL of 1 M $AgNO_3$ aqueous solution and 0.1 mL of 0.25 M lactic acid, succinic acid, or camphorsulfonic acid for 30 min. Here, for comparison, Ag growth on doped PANI membranes in just $AgNO_3$ solution was also carried out. After Ag growth, the PANI membranes were washed by water thoroughly, and dried in air.

Characterization. Scanning electron microscopy (SEM) images were taken on a FEI Inspect SEM. The characteristics of the crystallite structure of the prepared samples were determined using an XRD-6000 X-ray diffractometer (Shimadzu) with a Cu Kα radiation source (λ = 1.5405 Å, 40.0 kV, and 30.0 mA). Static contact angles were measured by placing droplets of deionized water (~2 mm in diameter) on the PANI surface. For SERS measurement, the PANI membranes after Ag growth were immersed in 4-MBA ethanol solutions of different concentrations for 30 min, and then washed with ethanol thoroughly. The Raman spectra were recorded on a Thermo Fisher Smart Raman instrument (wavelength: 785 nm). The incident laser power was kept at 5 mW, and total accumulation times of 2 s were employed.

III. RESULTS AND DISCUSSION

As stimulated by our previous result, that a very small amount of organic acid added into the $AgNO_3$ solution can lead to homogeneous Ag nanostructures that are inaccessible in just $AgNO_3$ solution on PANI membranes prefabricated with a Au nanolayer,[22] we tried Ag growth on undoped PANI membranes in a mixture solution of $AgNO_3$ and succinic acid, lactic acid, and camphorsulfonic acid. As shown in Figure 1, only scattered Ag nanostructures were obtained. From the solution with succinic acid, flowerlike Ag nanostructures ~1 μm in size, which are assembled by Ag nanosheets, are produced (see Figures 1a and 1b). With the addition of lactic acid (Figures 1c and 1d), Ag nanoparticles that are 100−200 nm in size with a mixed morphology are grown on the undoped PANI membrane. For camphorsulfonic acid, very huge Ag sheets that are several micrometers in size are achieved (Figures 1e and 1f). This result may indicate that, on undoped PANI membranes, it is not able to get fully covered Ag nanostructures simply by adding organic acid into the $AgNO_3$ solution.

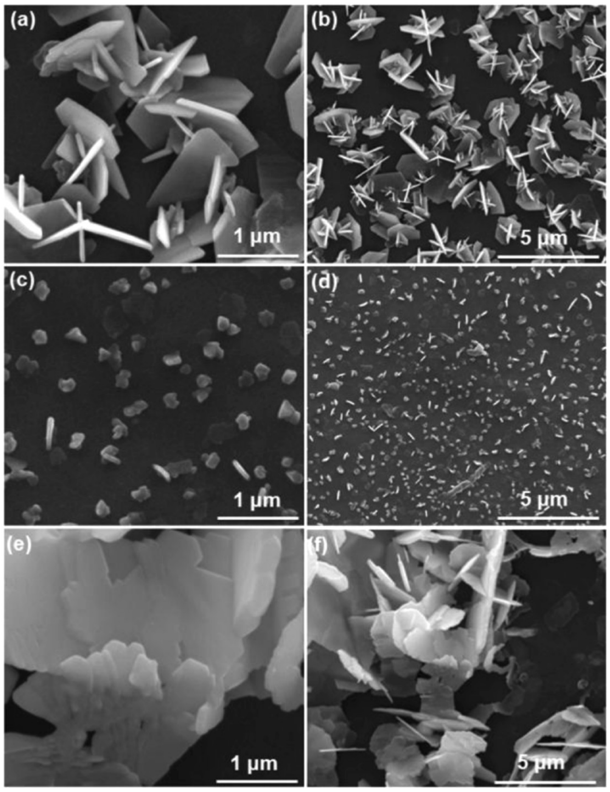

Figure 1. SEM images of silver nanostructures produced on the undoped PANI membranes, with (a, b) succinic acid, (c, d) lactic acid, and (e, f) camphorsulfonic acid present in the $AgNO_3$ solution.

It is surprising to find that, on doped PANI membranes, the same procedures that have been performed can lead to homogeneous Ag nanostructures with greatly improved surface coverage on the PANI surface (Figure 2). However, the morphology and surface coverage of the Ag nanostructures are sensitive to the category of the acid added in the $AgNO_3$ solution. The Ag nanostructures obtained with the addition of succinic acid and lactic acid are both assemblies of Ag nanosheets, which fully covered the PANI surface. Upon close examination, they are different Ag nanosheet structures. With the assistance of succinic acid (Figures 2a and 2b), one can see rigid Ag nanosheets with a thickness of ~70 nm, resembling the Ag nanosheet on undoped PANI membrane. With lactic acid in the $AgNO_3$ solution, one can get assemblies of flexible Ag nanosheets with larger sizes but smaller thicknesses (Figure 2c). In addition, several of these flexible Ag nanosheets can be bundled together, as indicated by the arrows in Figure 2d. While, with camphorsulfonic acid in the $AgNO_3$ solution, we only get scattered Ag particles ~10 μm in size (Figure 2e). From the magnified image in Figure 2f, one can see that these big particles are actually assemblies of Ag sheets and particles. When we perform the Ag growth on doped PANI membrane in just $AgNO_3$ solution, we only get scattered Ag particles, even after a reaction period of 1 h. (See Figure S1 in the Supporting Information.) Therefore, here, the Ag nanosheets with different sizes and structures should be due to the chemical nature of the acid added into the $AgNO_3$ solution.

One may easily raise the question about why so different Ag nanostructures are produced on the undoped and doped PANI membranes. First of all, as we discovered previously, it would

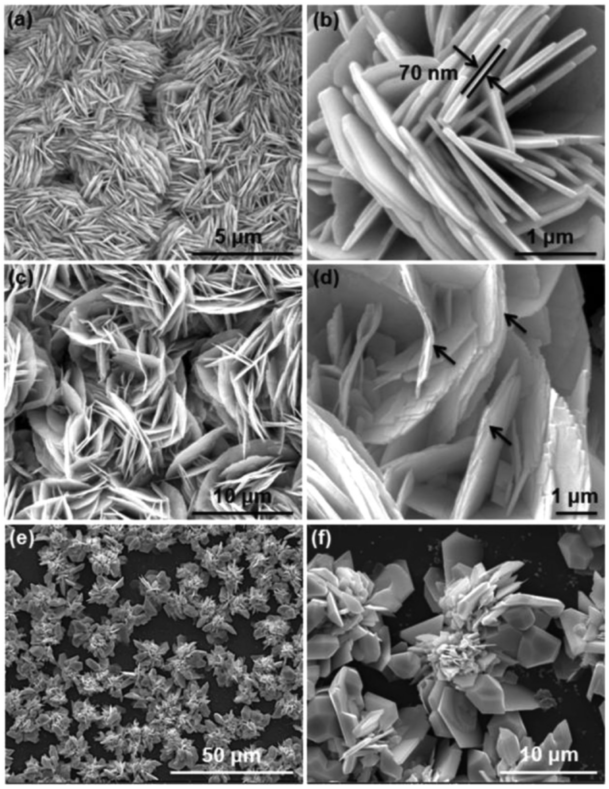

Figure 2. Scanning electron microscopy (SEM) images of silver nanostructures produced on the camphorsulfonic-acid-doped PANI membranes, with (a, b) succinic acid, (c, d) lactic acid, and (e, f) camphorsulfonic acid present in the $AgNO_3$ solution.

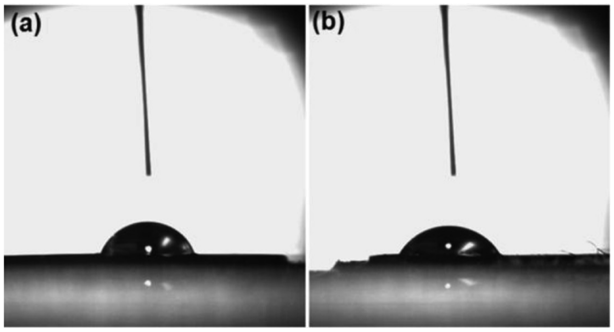

Figure 3. Surface wettability comparison of undoped (a, contact angle = 72.3°) and doped (b, contact angle = 60.1°) PANI membranes, measured by placing droplets of deionized water on the PANI surface.

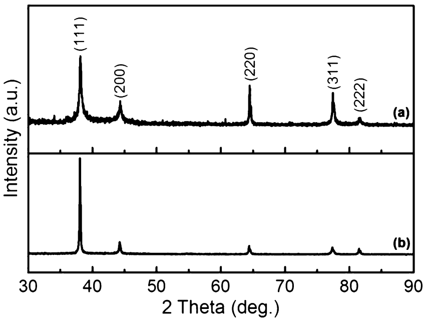

Figure 4. X-ray diffraction (XRD) patterns of silver nanostructures produced on the camphorsulfonic-acid-doped PANI membranes, with (a) succinic acid and (b) lactic acid present in the $AgNO_3$ solution.

be very difficult to get homogeneous Ag nanostructures on undoped PANI surfaces,[22,23] since doping with acid could render a homogeneous nucleation environment over the entire PANI surface, and hence a greater chance to get Ag nanostructures fully covering the PANI membranes. With acid in the $AgNO_3$ solution, in situ doping will be happening when the PANI membranes are immersed in the mixture solution, which, however, is not enough to create a homogeneous nucleation condition for the Ag growth over the entire PANI surface on undoped samples. Also, the chemical nature of the acid added into the $AgNO_3$ solution is critical to the morphology and surface coverage of Ag nanostructures on the PANI surface, where, in this case, succinic acid and lactic acid lead to homogeneous Ag nanostructures fully covering the PANI surface. Second, Ag growth on PANI membranes is a process of surface chemistry, and thus surface wettability will also play an important role for the nucleation of Ag seeds. As shown in Figure 3, we found that the doping process did change the contact angle of water on undoped (72.3°) and doped (60.1°) PANI membranes, which means that doped samples have better wettability in aqueous solutions. We think this also helps to create the improved surface coverage of Ag nanostructures on doped PANI membrane surfaces.

Here, we are particularly interested in the Ag nanostructures that are actually assembled by different types of nanosheets produced with the assistance of succinic acid and lactic acid. As seen from the XRD patterns of both samples (Figure 4), the diffraction peaks can be well indexed to the (111), (200), (220), (311), and (222) crystal planes of face-center-cubic (fcc) Ag crystals. However, it is calculated that the intensity ratio of (111) and (200) planes, $I(111)/I(200)$, is 3.75 and 8.02 for the Ag nanostructures produced with the assistance of succinic acid and lactic acid, respectively, which is ~2.0 for bulk Ag crystals.[28] This indicates that these Ag nanosheets are preferably grown along the (111) direction, especially for the flexible Ag nanosheets obtained with lactic acid in the $AgNO_3$ solution. High-resolution transmission electron microscopy (HRTEM) images also confirm that [111] planes are dominant in these nanosheets. (See Figure S2 in the Supporting Information.) Very different $I(111)/I(200)$ values for the Ag nanostructures from succinic acid and lactic acid again validate that acid introduced in the $AgNO_3$ solution will affect the nucleation and growth of Ag.

4-Mercaptobenzoic acid (4-MBA), an organic molecule with a thiol group on one end and a carboxylic acid on the other end, which has strong chemical interactions with metal surfaces, is selected as the target analyte to study the SERS sensitivity of different Ag nanostructures. The SERS spectrum of 4-MBA is dominated by the ν_{8a} (~1590 cm^{-1}) and ν_{12} (~1080 cm^{-1}) aromatic ring vibrations; other weak bands at ~1150 and ~1180 cm^{-1} are attributed to the C−H deformation modes.[29] As tested, the substrates are relatively very clean before being used for SERS detection of target molecules. (See Figure S3 in the Supporting Information.) As shown in Figure 5, on the big Ag particles grown on doped PANI membrane with the assistance of camphorsulfonic acid (see Figures 2e and 2f), well-resolved Raman spectra of 4-MBA can be obtained at concentrations of 10^{-2} and 10^{-4} M. Further decreasing the MBA concentration ($<10^{-6}$ M), the background noise becomes comparable to the signal, which verifies our previous result that, with bare PANI uncovered by Ag, it is normal to find Raman

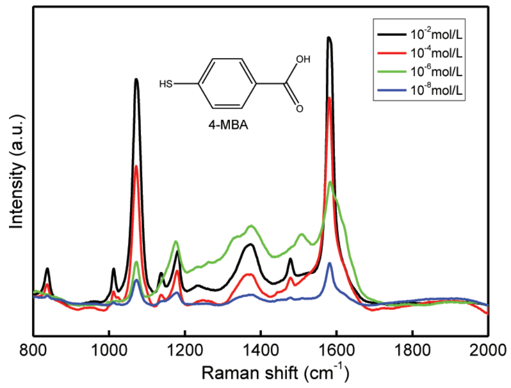

Figure 5. Concentration-dependent SERS spectra of 4-MBA taken from the Ag nanostructures produced on the doped PANI membranes with camphorsulfonic acid present in the $AgNO_3$ solution (see Figures 2e and 2f).

signals strongly influenced by the noise when the analyte concentration is really low.[22]

Impressively, when Ag nanostructures fully covering the PANI surface are applied for the SERS detection of 4-MBA, the sensitivity is extremely high, where 4-MBA with a concentration of 10^{-12} M can be easily tracked (Figure 6). From a 4-MBA concentration of 10^{-2} M to 10^{-12} M, we can see very sharp MBA peaks with very limited noise. Further decreasing the concentration to 10^{-14} M, Raman signals of 4-MBA cannot be tracked on the current substrate. Using the substrate prepared with the assistance of lactic acid leads to similar result that detection limit is up to 10^{-12} M. (See Figure S4 in the Supporting Information.) Moreover, our substrates show very nice uniformity of SERS responses when we collect the Raman spectra of the target molecule at different positions on one same substrate. (See Figures S5 and S6 in the Supporting Information.) From the relationship between concentration of 4-MBA and Raman intensity at 1582 cm^{-1} shown inset in Figure 6, one can see a linear increase of the Raman intensity with increasing 4-MBA concentrations from 10^{-12} M to 10^{-6} M. This means that when the concentration is lower than 10^{-6} M, all 4-MBA molecules adsorbed on the Ag surface are "enhanced" equally, since there are enough "hot spots" for these molecules. However, it can be seen that with higher concentration (10^{-4} M), the enhancement of the Raman intensity is actually decreased, which can rationalized by the fact that when a large amount of 4-MBA molecules are adsorbed on the Ag structures, some molecules may locate at the spots that are not so hot and molecule overlapping may also occur; therefore, the averaged enhancement factor will be decreased.

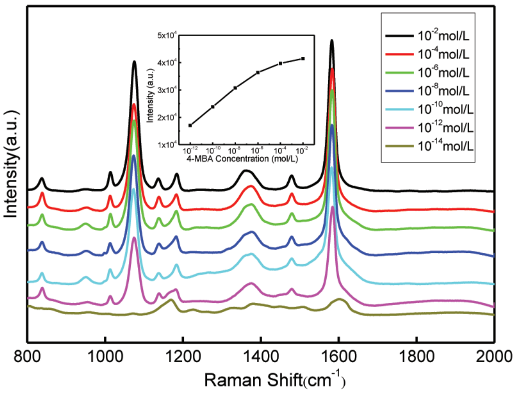

Figure 6. Concentration-dependent SERS spectra of 4-MBA taken from the Ag nanostructures produced on the doped PANI membranes, with succinic acid present in the $AgNO_3$ solution (see Figures 2a and 2b). Inset shows the relationship between Raman intensity at 1582 cm^{-1} and concentration of 4-MBA.

IV. CONCLUSIONS

In summary, we have demonstrated an improved technique to fabricate homogeneous Ag nanostructures fully covering the PANI membrane surfaces by introducing proper organic acid in the $AgNO_3$ solution. However, it is found that introduction of organic acid in the $AgNO_3$ solution cannot lead to Ag nanostructures fully covering the undoped PANI membranes. Of note is that the chemical nature of the added acid plays a dominant role in the morphology and surface coverage of the Ag nanostructures grown on the PANI surface. In our case, Ag nanostructures that are assembled by Ag nanosheets are obtained with the assistance of succinic acid and lactic acid, which cover the entire PANI surface. Also, we think the improved surface wettability of doped PANI membrane should account for the higher coverage of Ag nanostructures. The Ag nanostructures fully covering the PANI surface show extremely high sensitivity in SERS detection of the target analyte, 4-MBA, with a detection limit up to 10^{-12} M, which is not accessible or tested in our previous works. We believe this improved yet facile technique to fabricate homogeneous Ag nanostructures on top of the PANI membrane surface may open up a new avenue for fabricating highly sensitive SERS-active substrates for the detection of trace amount of chemical and biological molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM images, HR-TEM images, and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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