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Fast fabrication of homogeneous Ag nanostructures on dual-acid doped polyaniline for SERS applications

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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We demonstrate a dual-acid doping technique for PANI membranes, which enables fast fabrication of homogeneous Ag nanostructures as SERS-active platforms for chemical detection. Ascorbic acid, an intrinsic reducing agent, can accelerate the Ag growth, and succinic acid plays the role of controlling the morphology of the Ag nanostructures. When ascorbic acid is used alone, bulk Ag particles are obtained, which show relatively poor SERS sensitivity (10^{-5} M) towards the target analyte, methylene blue (MB). Homogeneous Ag nanostructures assembled by nanosheets can be fabricated on dual-acid doped PANI membranes within 2 min. These Ag nanostructures are extremely sensitive towards both target molecules, Rhodamine B (RhB) and MB, with a detection sensitivity of 10^{-10} M. The as-fabricated SERS platforms can also be applied for semi-quantitative determination of the carcinogenic RhB in juice. We believe the highly sensitive SERS platforms can be promising in the trace detection of chemical and biological molecules.

1. Introduction

Surface-enhanced Raman spectroscopy (SERS) primarily utilizes the greatly enhanced electromagnetic field as well as the localized surface plasmon resonances generated at metal surface to enhance the Raman signals of target molecules.[1-3] SERS can serve as a highly sensitive probe for trace detection of chemical and biological molecules up to a single molecule level,[4-6] and a powerful technique that can be applied in food safety, environmental and biomedical science.[7-9] To date, various SERS substrates have been reported, such as metal nanoparticle assemblies,[10-13] roughened metal substrates,[14-17] porous or holey substrates[18-20] and even semiconductor-based substrates.[21-24] However, SERS substrates should be reproducible, facile for fabrication, highly sensitive, and site-independent of "hot spots", while the great majority of above-mentioned substrates require relatively complicated and cost-ineffective manipulations.

Recent works have demonstrated that noble metals such as Au, Ag, Pt, Pd can be spontaneously grown on polyaniline(PANI) surfaces through a direct chemical deposition technique,[25-28] where the size and morphology of the metal nanostructures can be simply controlled by the surface chemistry and chemical nature of PANI, and reaction conditions like temperature, metal salt concentration, reaction time.[25-28] The as-fabricated Ag and Au nanostructures with well-defined morphologies have shown promises as highly efficient and cost-effective SERS substrates for chemical detection. It is also found that PANI membranes treated by hydrazine can be utilized for fast fabrication of homogeneous Ag nanostructures fully covering the PANI surfaces, but directing acid added to $AgNO_3$ solution is indispensable for size and morphology control of Ag.[25] In the attempt to fast fabrication of Ag structures on PANI surface, we are very interested in applying ascorbic acid, widely used as a reducing agent for the facile and fast preparation of the noble metal nanoparticles, as a doping acid for the PANI membranes.

Herein, we demonstrate a fast fabrication method (~ 2 min) of homogeneous Ag nanostructures on dual-acid (ascorbic acid and succinic acid) doped PANI membranes. Our previous in situ doping process of PANI usually requires a relatively longer time period (~ 1 h) to obtain Ag nanostructures fully covering the PANI surface.[3] This dual-acid doping technique, combining the reducing nature of ascorbic acid and directing effect of Ag growth by succinic acid, renders a fast growth of Ag on PANI as well as an easy control of the morphology and homogeneity of the Ag nanostructures. The Ag nanostructures show highly sensitive SERS response to the selected dye target analytes, Rhodamine B (RhB) and methylene blue (MB), with a detection limit of 10^{-10} M. Moreover, the Ag/PANI SERS platforms can also be used for semi-quantitative determination of the carcinogenic RhB in juice. We believe this fast and facile fabrication of Ag nanostructures on PANI surfaces can be promising in preparing highly efficient SERS platforms for the detection of chemical and biological molecules.

2. Experimental

Materials: PANI emeraldine base (EB) powder (Aldrich), *N*-Methyl-2-pyrrolidone (NMP, 99% Aldrich), heptamethyl-enimine (HPMI, 98% Acros), $AgNO_3$ (99.9%, Sinopharm Chemical Reagent Co., Ltd.), ascorbic acid (AA, $C_6H_8O_6$ 99.8%, Sinopharm Chemical Reagent Co., Ltd.), succinic acid (SA, >99.5% Fisher), Rhodamine B (RhB, Aldrich), and methylene blue (MB, Aldrich) were used as received.

Fabrication of PANI Membranes: PANI membranes are fabricated by a phase inversion method using water as the coagulation bath.[2] 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 of 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 PANI membrane will be peeled off from the glass substrate spontaneously during the solvent exchange process. The resulting membrane was then dried at room temperature for 6 h, and then cut into 5 mm × 5 mm pieces. The small PANI pieces were treated in 0.25 M AA, or a mixture of 0.25M AA and SA for 2 days, after which the PANI pieces were washed with water repeatedly and thoroughly to remove any acid residual.

Growth of Ag nanostructures: For the preparation of Ag nanostructures, one doped PANI piece was immersed in 1 ml of 0.1 M $AgNO_3$ solution, where Ag can be immediately grown on the PANI surface. Here, Ag growth was lasted for 30 s, 1 min, 2 min and 5 min to study the morphology evolution. After Ag growth, the PANI pieces were washed with distilled water repeatedly to remove any $AgNO_3$ residual, and dried in air.

Characterization: Scanning electron microscopic (SEM) images were taken on a FEI Inspect SEM. The X-ray diffraction (XRD) measurements were carried out on a Shimadzu XRD-6000 diffract meter using fine line sealed Cu-Kα tube (λ= 1.5406 Å) X-rays. For SERS measurement, the Ag-supported PANI membranes were immersed in RhB and MB aqueous solutions of different concentrations for 30 min, and then washed with deionized water thoroughly. The SERS spectra were recorded on a Renishaw In Via micro Raman spectroscopy system, using the TE air-cooled 576 × 400 CCD array in a confocal Raman system (wavelength: 633 nm).

Detection of RhB in juice: The commercially obtained juice was centrifuged to remove the pulp before adding 0.1 ml RhB aqueous solution of different concentrations to each 5 ml of juice. Then 10 μL of the solution were dropped onto the as-prepared Ag/PANI membranes. After being dried in air, SERS measurement were carried out.

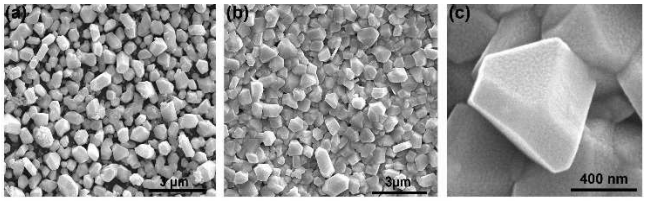

Fig. 1 SEM images of Ag particles grown directly on AA-doped PANI membranes for (a) 1 min and (b, c) 2 min.

3. Results and discussion

As stimulated by our previous results,[25,28] reducing agent (hydrazine) treatment can accelerate the Ag growth and acid doping contributes greatly to the coverage and morphology of Ag nanostructures on PANI substrates. Since ascorbic acid (AA) is one common reducing agent and proton acid, we are very interested in doping the PANI membranes with AA to study the Ag growth. AA doping did accelerate the Ag growth on PANI surface as we saw on hydrazine doped PANI films,[25] however, only bulk Ag materials without any morphology features were produced after immersing the AA doped PANI membrane into 0.1 M $AgNO_3$ solution. Although we only get bulk Ag particles on AA doped PANI substrates, it is important to realize the fact that Ag particles fully covering the PANI surface can be achieved in a very short time (less than 2 min). As shown in Fig. 1a, at 1min, irregular polyhedral Ag particles that are about 500 nm in size can be obtained on AA-doped PANI surfaces. When the reaction time is prolonged to 2 min, as shown in Fig. 1 b, c, the size of the Ag particles remains almost identical, but PANI membrane surface are more densely covered.

To study the SERS responses of the as-prepared Ag particles, methylene blue (MB) is selected as the target molecule here. In order to clarify that there is no influence from the substrate in SERS detection, we compared the Raman spectra of pure Ag/PANI and MB on Ag/PANI (see Fig. S1 in ESI†). It has been found that the Raman feature of pure Ag/PANI is relatively weak, and there is no overlap between the Raman peaks from the substrate and MB. This means the substrate we made is relatively clean and appealing for SERS detection. Raman spectrum of MB is dominated by ν(C-C) ring stretching at 1618 cm^{-1}, α(C-H) in-plane ring deformation at 1398 cm^{-1}. As seen in Fig. 2, it is able to detect MB molecules at a concentration of 10^{-5} M (ppm level) on the Ag particles prepared on AA-doped PANI at a reaction time of 2 min. Since SERS "hot spots" often reside in metal structures with bifurcations or intersections, and the interstitial voids of metal nanoparticles, and high radius of curvatures, it is not surprising to see that the bulk Ag particles (see Fig.1) with neither sharp edges or corners serving as SERS "hot spots" nor large surface area to adsorb analysts show relatively poor SERS sensitivity.

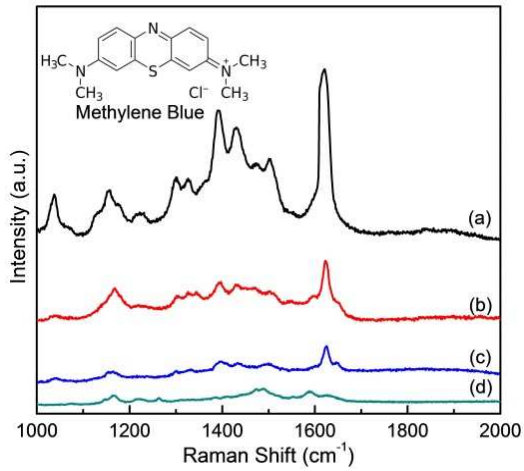

Fig. 2 SERS spectra of MB adsorbed on Ag nanostructures supported on AA-doped PANI membranes at a reaction time of 2 min. (a) 10^{-3} M, (b) 10^{-4} M, (c) 10^{-5} M, and (d) 10^{-6} M.

Since only bulk Ag particles with poor SERS sensitivity are fabricated on AA-doped PANI membranes, we immediately think of the acid-directed routes: using AA to accelerate the Ag growth and another acid to control the morphology of the Ag nanostructures. We call this dual-acid doping technique to the PANI substrates. Fig. 3 shows the Ag nanostructures on PANI membranes doped by AA and succinic acid (SA) at different reaction times. As shown in Fig. 3a, a reaction time of 30 s leads to evenly distributed Ag nanostructures over the whole PANI surface with visible bare PANI that is not covered by Ag, and a close examination shows that they are composed of Ag nanoparticles and nanosheets with a thickness of about 50 nm (Fig. 3b). At 1 min, the morphology of the Ag nanostructures is dominated by clustered nanosheets (Fig. 3c). A magnified SEM image indicates that these nanosheets are about 100 nm in

thickness (Fig. 3d). The black holes at the interstitial parts of the clusters tell that at this stage the PANI surface is still not fully covered by Ag structures, which has been found to affect the SERS response on such metal/polymer substrates. When the reaction time is prolonged to 2 min, as shown in Fig. 3e, Ag nanosheet structures that fully cover the PANI surface can be obtained, and a close look at these nanosheets reveals that they are randomly stacked with slightly larger thickness (~150-200 nm). At 5 min, these randomly distributed Ag nanosheets grow even thicker, reaching 200-300 nm, as shown in Fig. 3 g and h. As compared to a previous report,[2] this dual-acid doping technique can greatly accelerate the Ag growth and produce SERS favorable morphologies simultaneously.

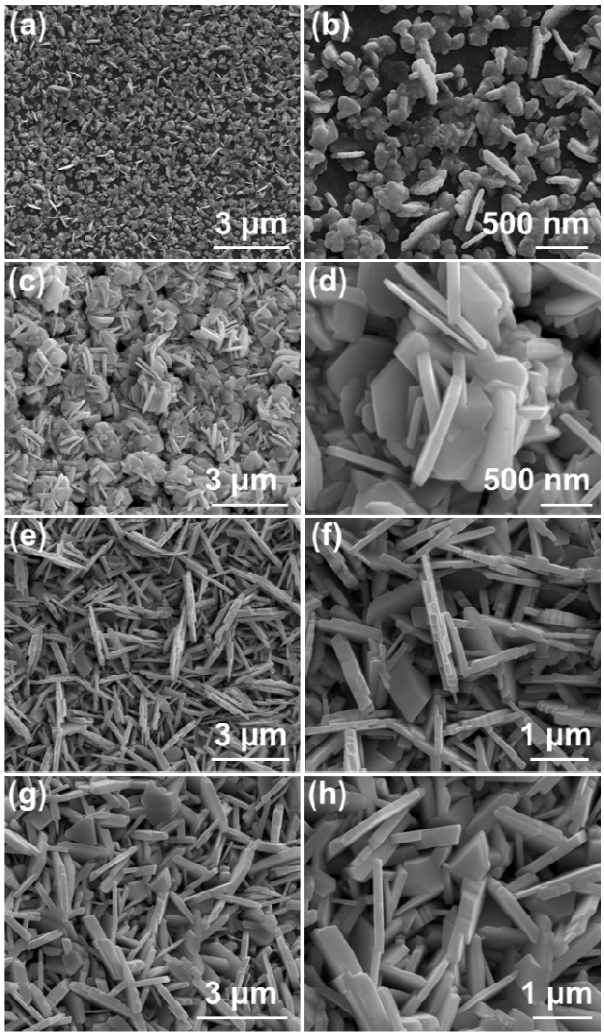

Fig. 3 SEM images of the Ag nanostructures grown on dual-acid (AA and succinic acid) doped PANI membranes for different reaction periods: (a, b) 30 s; (c, d) 1 min; (e, f) 2 min; (g, h) 5 min.

It should be noted that these Ag nanosheet structures resemble the morphology we obtained on PANI surface when succinic acid (SA) is present in the $AgNO_3$ solution,[3] which highly implies that SA used in this dual-acid doping process plays the role of morphology control of the Ag structures. Taking the above results together, we can tell that AA doping facilitates the Ag growth and SA directs the structure evolution, which exactly fulfills our design in the dual-acid doping technique. It is found that using lactic acid (LA) to substitute SA can also lead to well-defined Ag nanostructures fully covering the PANI surface in a short time period (see Fig. S2 in ESI†), where LA controls the morphology of the Ag structures. However, this dual-acid doping technique is not universal to all organic acids, as we found using mandelic acid to substitute SA only results in the bulk Ag particles similar to those obtained on PANI membranes doped just by AA (see Fig. S3 in ESI†). Interestingly, Ag structures on PANI membranes doped by AA and citric acid are bulk particles whose surfaces are decorated with tiny nanosheets mimicking the effect of citric acid doped PANI membranes (see Fig. S4 in ESI†).[2] Therefore, we believe there is a competing effect between the two acids used to dope the PANI membranes, according to structures of the acid molecules. If the PANI chain is doped dominantly by AA, leaving very limited or no space for the second acid, the Ag structures obtained on PANI membranes should be just bulk particles. However, when both acids (AA and the other one) have relatively enough chance to dope PANI, the as-designed dual-acid doping technique will function as a fast fabrication of well-defined Ag nanostructures on PANI surfaces. Nevertheless, above results have demonstrated that it is possible to grow Ag nanostructures with controlled morphology in a very short time period through this dual-acid doping process.

XRD patterns of the Ag particles fabricated on AA and AA-SA doped PANI surfaces are shown in Fig. 4. The diffraction peaks can be well indexed to the (111), (200), (220), (311), and (222) crystal planes of face-centered-cubic (fcc) Ag crystals. However, the intensity ratios of (111) to (200) planes, $I(111)/I(200)$, are 2.79 and 6.28 for the Ag structures fabricated on PANI surfaces doped by AA and AA-SA, respectively, which is usually about 2.0 for bulk Ag crystals. This result indicates an isotropic growth of Ag particles on AA doped membranes, leading to bulk Ag. While, anisotropic growth along (111) orientation occurs on AA-SA doped PANI membranes. As for the growth mechanism, we think it can be rationalized by the fact that AA here plays the role of accelerating the Ag growth, while SA dominates the growth orientation (morphology control) of the Ag nanostructures. When Ag ions are quickly reduced by AA doped PANI, SA molecules might be moved and adsorbed on the Ag nuclei face and direct the Ag growth along the (111) crystal plane. Similar results have also been reported by other groups.[29]

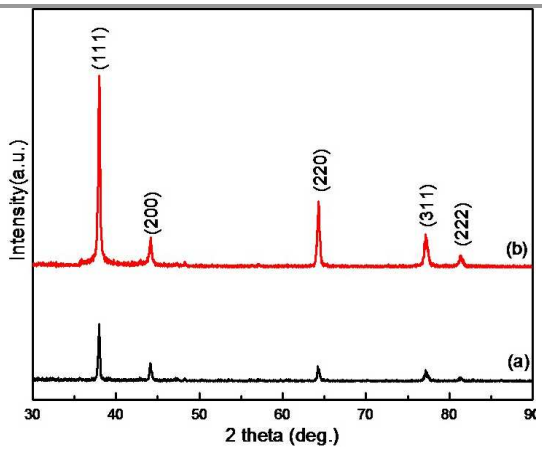

Fig. 4 XRD patterns of the Ag structures fabricated on the PANI membranes doped by (a) ascorbic acid and (b) dual acid (ascorbic acid-succinic acid).

We use Rhodamine B (RhB) and MB as target molecules to measure the sensitivity and generality of those Ag nanostructures for SERS applications. Since SERS response can be greatly influenced by the metal nanostructures,[30] we have compared the SERS spectra of MB on Ag nanostructures prepared at different time periods (see Fig. S5 in ESI†). It has been found that the Ag nanosheets prepared at 2 min shows the most enhanced Raman signals. Therefore, we mainly studied the SERS responses on Ag nanosheets fully covering the PANI surface at a reaction time of 2 min (see Fig. 3 e and f). Raman spectrum of RhB is dominated by ν (C-H in plane) (1287 cm^{-1}) and ν(Arom C-H) (1647, 1507, 1362, 1199 cm^{-1}) and ν(C-H) (1530 cm^{-1}).[4] As shown in Fig. 5, the Ag nanostructures fabricated on AA-SA doped PANI substrates at 2 min are able to detect RhB at a concentration of 10^{-10} M, which is a considerable improvement as compared to the Ag bulk particles fabricated on AA doped PANI membranes. Surfactants like PVP, CTAB are often used to prepare well-defined metal nanostructures, which are inevitable to be absorbed onto the surface of metal nanoparticles.[31, 32] Surfactant absorption will reduce the surface area of metal nanoparticles, and even disturb the absorption of target molecules for SERS detection. We believe cleaner surfaces and higher surface areas of Ag nanostructures fabricated on AA-SA doped PANI membranes are responsible for the higher SERS sensitivity. Homogeneous Ag nanosheet-assembled film fabricated from galvanic replacement with Cu_2O showed a detection limit of R6G up to 10^{-12} M,[30] which could be ascribed to the hierarchical structures with a denser coverage. In one of our previous works,[3] the Ag nanosheet assemblies fabricated on PANI surface through an in situ doping process showed a detection sensitivity of 10^{-12} M of the target molecules. As SERS response is very sensitive to the detail structures of the metal nanoparticles, we believe the SERS enhancement from various substrates differs from the metal nanostructures as well as the chemical nature of the target molecules. On the Ag nanostructures fabricated on AA-SA doped PANI substrates at 2 min, we are also able to detect MB molecules at a sensitivity of 10^{-10} M (see Fig. S6 in ESI†), which indicates the generality of using such Ag nanostructures as SERS-active substrates for chemical detection.

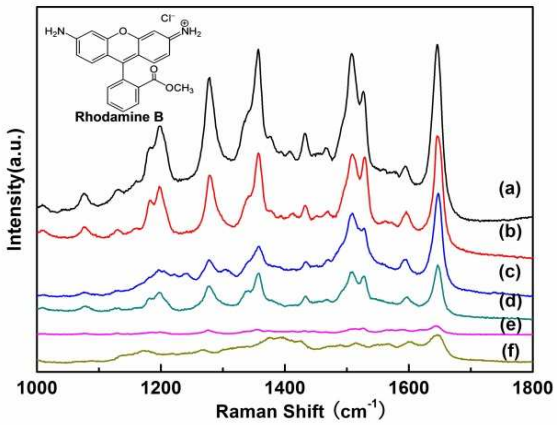

Fig. 5 SERS spectra of RhB on Ag nanostructures supported on AA-SA doped PANI membranes at a reaction time of 2 min. (a) 10^{-4} M, (b) 10^{-6} M, (c) 10^{-8} M, (d) 10^{-9} M, (e) 10^{-10} M, and (f) 10^{-11} M.

We also applied the as-prepared SERS-active platforms for the detection of carcinogenic RhB in juice. As can be seen form the optical images of the right panel inset in Fig. 6, juice mixed with RhB at a concentration of 10^{-5} M almost has the same color as the pure juice, indicating that it is not able to distinguish the presence of RhB at such a concentration by bare eyes. Importantly, as shown in Fig. 6, SERS detection of RhB in juice can reach 10^{-7} M, a value that is at least two orders of magnitude lower than that we can distinguish by bare eyes. However, currently we are not able to detect RhB molecules in juice at even lower concentrations, presumably due to the influence of juice components. The peak at 1647 cm^{-1} is used as for quantitative analysis of the concentration of RhB in juice. As shown in left panel inset in Fig. 6, with a concentration lower than 10^{-5} M, the Raman intensity and concentration of RhB in juice display an almost linear relationship, which is very useful to determine the content of dyes like RhB in juice. Given an unknown juice, the content of RhB molecules can be determined by measuring the SERS spectra after dilution till the Raman intensity falls into the linear region. We have carried out repeating experiments in measuring the SERS spectra of RhB in juice, and the linear relationship can be well maintained at concentrations lower than 10^{-5} M. These results indicate that the as-prepared SERS substrates can also be applied for semi-quantitative detection of dyes in juice, which is of great significance for food safety.

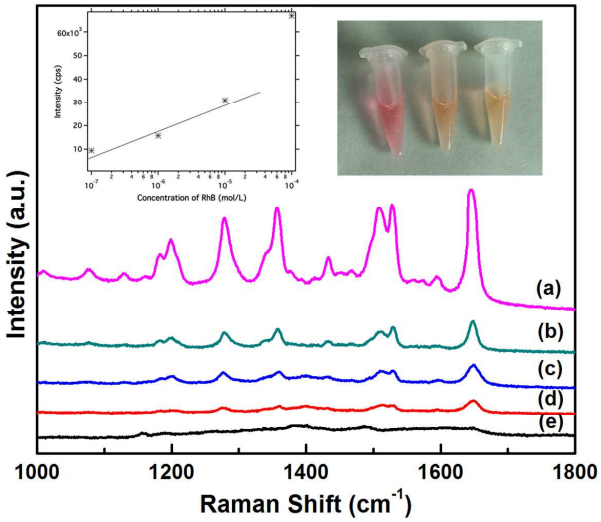

Fig. 6 SERS spectra of RhB in juice with concentrations of (a) 10^{-4}, (b) 10^{-5}, (c) 10^{-6}, and (d) 10^{-7} M. (e) SERS spectra of the juice. Left panel in inset: relationship between Raman intensity of the peak at 1647 cm^{-1} and concentration of RhB in juice. Right panel in inset: optical images of juice with RhB at a concentration of 10^{-4} M (left), 10^{-5} M (middle) and pure juice (right).

4. Conclusions

In summary, we demonstrate here a facile and fast fabrication of homogeneous Ag nanostructures assembled by nanosheets simply by doping the PANI films with dual-acid (succinic acid and ascorbic acid). Bulk Ag particles are obtained on the PANI surfaces doped only by ascorbic acid, which shows poor SERS activities due to the lack of hot spots. Homogeneous Ag nanostructures fully covering the membrane surface can be efficiently fabricated on AA-SA doped PANI substrates in 2 min, which are extremely sensitive to both selected target analyte (up to 10^{-10} M), Rhodamine B and methylene blue. The rougher and cleaner surfaces of the Ag nanostructures should be responsible for the impressive SERS sensitivity. The as-fabricated SERS platforms can be applied for semi-quantitative determination of the carcinogenic RhB in juice. We believe this

facile and fast technique to fabricate homogeneous Ag nanostructures on top of the PANI surfaces may open up a new avenue for fabricating highly sensitive SERS-active platforms for the detection of trace amount of chemical and biological molecules.

Acknowledgements

PX thanks support from the China Postdoctor Fund, NSFC (No. 21203045, 21101041, 21003029, 21071037, 91122002), Fundamental Research Funds for the Central Universities (No. HIT.NSRIF. 2010065 and 2011017, and HIT.BRETIII.201223), and the 9th Thousand Foreign Experts Program.

Notes and references

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† Electronic Supplementary Information (ESI) available: Fig. S1-S6. See DOI: 10.1039/b000000x/

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