Electronic Supplementary Information (ESI)

Fast fabrication of homogeneous silver nanostructures on hydrazine treated polyaniline films For SERS applications

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Experimental:

Fabrication of the PANI films: A typical procedure of fabricating the PANI film is described as follow: 4.14 g of N-Methyl-2-pyrrolidone (NMP), 0.747 g of heptamethylenimine (HPMI), and 1.15 g of PANI (EB) powder 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 (Pompano Beach, FL) with a controlled thickness. The wet film was put in an oven at 50 °C for 12 h to evaporate the solvent and form a dense film. The dried film was kept in a water bath to let it peel off from the glass substrate. The resulting film was dried in air and cut into 5 mm × 5 mm pieces. The small PANI pieces were then put into a 10% hydrazine aqueous solution for 0.5 h, after which the PANI pieces were washed with water repeatedly and thoroughly to remove any hydrazine residual.

Growth of silver nanostructures: For the preparation of silver nanostructures, one hydrazine treated PANI film was immersed in 0.1 ml of directing acid and 1 ml of 0.1 M AgNO₃ solution, where Ag can be immediately grown on the PANI film 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 films were washed with water repeatedly and thoroughly to remove any AgNO₃ residual, and dried in air.

Characterization: Scanning electron microscopic (SEM) images were taken on a FEI Inspect SEM. XRD patterns were recorded on an XRD-6000 X-ray diffractometer. The Ag-supported PANI films were immersed in 4-MBA ethanol solution of different concentrations for 30 min before the surface-enhanced Raman scattering (SERS) response was determined. 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.

Additional Images:

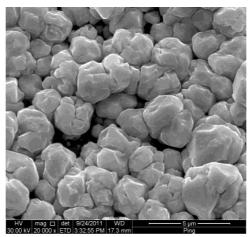


Fig. S1 SEM images of Ag nanostructures produced on hydrazine treated PANI films at a reaction time of 30 s, without any acid present in the 0.1 M AgNO₃ solution.

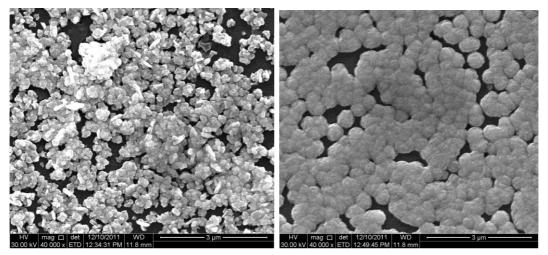


Fig. S2 SEM images of Ag nanostructures produced on hydrazine treated PANI films at a reaction time of 30 s, without salicylic acid (left), and citric acid (right) present in the 0.1 M AgNO₃ solution.

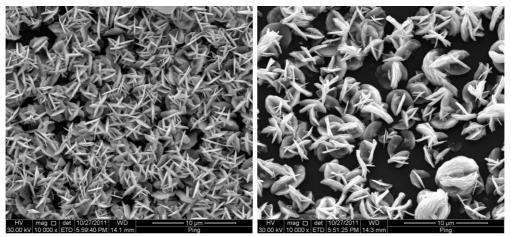


Fig. S3 SEM images of Ag nanostructures produced on undoped PANI films (without treated by hydrazine) at a reaction time of 10 min, with succinic acid (left), and lactic acid (right) present in the 0.1 M AgNO₃ solution.

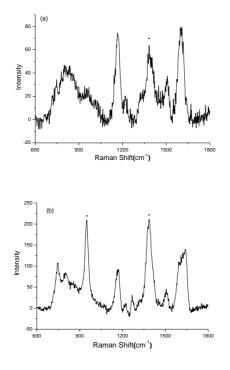


Fig. S4 Raman spectra directly taken on the Ag nanostructures produced on hydrazine treated PANI films with lactic acid (a) and succinic acid (b) present in the AgNO₃ solution. Here, the substrates were not immersed in 4-MBA solution. The asterisks indicate the Raman peaks of the acid, and the other peaks should be due to the PANI substrate. (Raman signal references: succinic acid: Journal of Molecular Spectroscopy 1968, 28, 394-410; lactic acid: Biopolymers 2006, 82, 286–290)

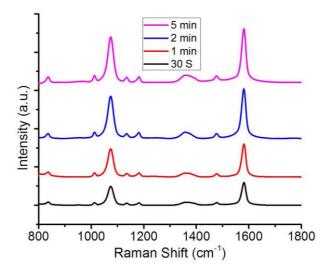


Fig. S5 SERS spectra of 4-mercaptobenzoic acid (4-MBA) with a concentration of 10^{-5} mol/L, taken on the Ag nanostructures produced on hydrazine treated PANI films at different reaction times with lactic acid present in the AgNO₃ solution.

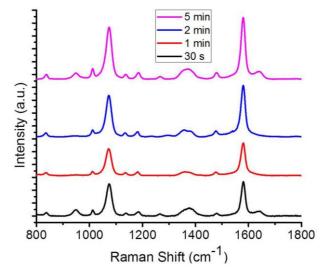


Fig. S6 SERS spectra of 4-mercaptobenzoic acid (4-MBA) with a concentration of 10^{-5} mol/L, taken on the Ag nanostructures produced on hydrazine treated PANI films at different reaction times with succinic acid present in the AgNO₃ solution.