

# Synthesis of homogeneous silver nanosheet assemblies for surface enhanced Raman scattering applications†

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Conducting polymers have been proved to be effective reducing agents in the synthesis of noble metal nanoparticles. We demonstrate here the fabrication of homogeneous Ag nanosheet assemblies on conducting polymer membranes with 5 wt% polyaniline (PANI) substituted by conductive additives like graphite (G) or multi-walled carbon nanotubes (CNTs). The inclusion of conductive additives that act as electrical connectors for the PANI particles changes the surface property and creates a homogeneous nucleation environment, leading to the membrane surface completely covered by the Ag nanosheet structures. The pack density of the nanosheets can be simply tuned by modulating the concentration of AgNO<sub>3</sub> aqueous solution. The as-prepared Ag nanosheet assemblies with abundant interstitial sites show strong SERS responses toward the mercaptobenzoic acid (MBA) molecules, with a detection sensitivity down to 5 ppm. A proper acid etching of these Ag nanosheet structures in 0.1 M HNO<sub>3</sub> aqueous solution makes the nanoparticles that form the nanosheets much more exposed to the analyte molecules, and an even stronger Raman enhancement can be obtained. We believe the homogeneous Ag nanosheet assemblies supported on conducting polymer membranes can be sensitive and cost-effective SERS substrates in molecule detection.

## Introduction

Surface-enhanced Raman scattering (SERS), which takes advantage of the strongly increased Raman signals generated by local field enhancement at metallic (typically Au and Ag) surfaces, is a powerful spectroscopic technique that can provide non-destructive and ultra-sensitive detection of chemical and biological molecules down to single molecular level.<sup>1–3</sup> It is commonly accepted that the enhancement is primarily due to highly concentrated electromagnetic fields associated with strong localized surface plasmon resonances at the so-called “hot spots” which often locate at those interstitial sites in nanostructures.<sup>4,5</sup> However, controlled synthesis of SERS “hot spots” remains difficult in most SERS active materials as it requires exquisite preparation of metal nanoparticles (MNPs) with controllable sizes and morphology and delicate manipulation of the nanoparticle assemblies.<sup>6,7</sup> Therefore, though a number of SERS substrates have been developed, fabrication of SERS-active substrates that have well-defined and reproducible structures is still greatly desirable for developing SERS sensors for efficient chemical, biological and medical applications.

Conducting polymers have been the subject of numerous investigations due to their potential in electronic and optical devices,<sup>8–10</sup> meanwhile, it is also recognized that a metal ion having a reduction potential higher than that of a conducting

polymer can be reduced by the conducting polymer to form zero-valent metal.<sup>11,12</sup> This opens up a new avenue for MNP fabrication, apart from the widely reported wet chemical solution. Palladium nanoparticles embedded onto polyaniline (PANI) nanofibers exhibit highly efficient catalytic functions in organic synthesis,<sup>13</sup> and PANI nanofiber/gold nanoparticle composites are recognized as an excellent component of a nonvolatile memory device.<sup>10</sup> In recent years, we have shown that PANI, polypyrrole (PPy), and their copolymers are all effective reducing agents that can be applied in chemical reduction of metal ions to produce MNPs.<sup>14–16</sup> Moreover, we also fabricate PANI particles into membranes and films, and it is found that MNPs (Ag, Au, Pt and Pd) can be directly deposited onto those membranes and films.<sup>17–20</sup> Interestingly, the morphology and size of the MNPs can be well controlled by tuning the chemical nature (acid dopant) of the PANI membranes and films.<sup>17</sup> We demonstrated in a very recent work that homogeneous three-dimensional (3D) Ag nanostructures produced on Au-supported PANI membranes could be promising SERS substrates.<sup>21</sup> However, we found that without pre-fabrication of a Au nanolayer on PANI membrane, only scattered Ag microspheres with poor surface coverage were obtained and the bare PANI uncovered by metal structures will severely reduce the SERS responses. Therefore, fabrication of homogeneous Ag nanostructures on conducting polymer substrates through a one-step process (direct chemical deposition of Ag) is highly expected. More importantly, compared with the metal structures fabricated on silicon substrates, Ag nanostructures fabricated onto conducting polymer substrates are much more cost-effective and attractive for SERS applications.

Here, we demonstrate a facile fabrication of homogeneous Ag nanosheet assemblies on conducting polymer substrates through a direct chemical deposition of Ag with PANI as the reducing

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agent. It is determined that inclusion of a small amount of conducting additive in the PANI membranes renders a homogeneous nucleation environment over the membrane surface, leading to membrane surface completely covered by uniform Ag nanosheet assemblies. The Ag nanostructures on conducting polymer substrates can be highly efficient SERS platforms, and a proper acid etching of the Ag nanosheets results in even stronger SERS responses.

## Experimental

### Materials

PANI emeraldine base (EB) (Aldrich), graphite (99%, Aldrich), multi-walled carbon nanotubes (Aldrich), *N*-Methyl-2-pyrrolidone (NMP, 99% Aldrich), heptamethyleneimine (HPMI, 98% Acros), AgNO<sub>3</sub> (99.9999% Aldrich), citric acid (99.9% Fisher), and mercaptobenzoic acid (MBA, Aldrich 90%) were used as received.

### Fabrication of conducting polymer membranes

The conducting polymer membranes are produced by employing a phase inversion method using water as the coagulation bath.<sup>17</sup> In a typical experiment of fabricating PANI membranes, 1.15 g PANI (EB) powder was placed in a 12 ml Teflon vial. Then 4.14 g of NMP and 0.747 g of HPMI were added. 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 then immersed into a water bath for 24 h, after which the resulting solid membrane was spontaneously delaminated from the glass substrate. The membrane was then dried at room temperature for 12 h before doping in 0.25 M citric acid for 3 days. In preparation of membranes with conducting additives, 5 wt% of PANI was substituted by graphite (G) or multi-walled carbon nanotubes (CNTs), with other procedures identical to those in preparation of PANI membranes, and the resulting membranes are called P-G and P-CNTs membranes.

### Growth of silver nanostructures

The citric acid doped membranes were cut into 5 mm × 5 mm pieces and immersed into freshly prepared aqueous AgNO<sub>3</sub> solutions. Metallic nanostructures immediately and spontaneously begin to form on the membrane surfaces. The doped conducting polymer membranes (PANI, P-G and P-CNTs) were placed in AgNO<sub>3</sub> solutions of different concentrations for different time to study the growth of silver nanostructures. After silver growth, the membranes were rinsed thoroughly with water to remove the adsorbed silver nitrate and dried in air.

### Acid etching

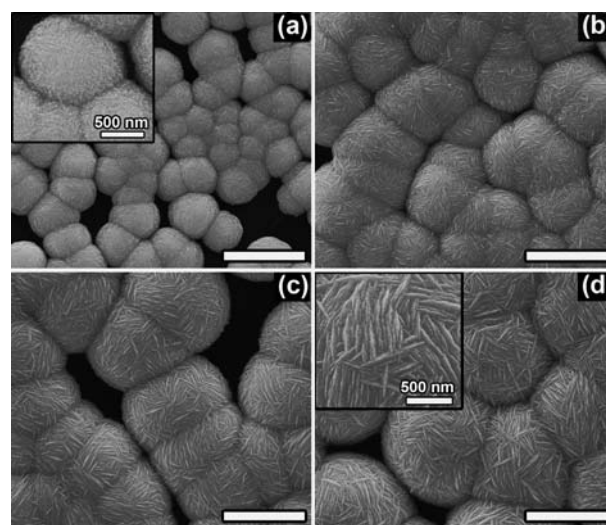
To get the acid etched silver nanostructures, silver supported P-G membranes were placed in 0.1 M HNO<sub>3</sub> aqueous solution for different time periods. After acid etching, the membranes were rinsed thoroughly with water to remove the adsorbed HNO<sub>3</sub> molecules. After rinsing, the metal supported conducting polymer membranes were dried in air.

## Characterization

Scanning electron microscopic (SEM) images were taken on an FEI Inspect F SEM to study the morphologies of the silver nanoparticles. The elemental composition was analyzed by energy-dispersive X-ray spectroscopy (EDAX), and X-ray diffraction (XRD) measurements were carried out on a Rigaku Ultima III diffractometer that uses fine line sealed Cu-K $\alpha$  tube ( $\lambda = 1.5406 \text{ \AA}$ ) X-rays. The metal-supported conducting polymer membranes were immersed in an MBA ethanol solution (4 mM) for 15 min and then rinsed in fresh ethanol prior to SERS measurements. The SERS spectra were taken on a Kaiser Raman spectrometer through a 20×(0.50 NA) microscope objective, coupled to a liquid-nitrogen-cooled charge-coupled device (CCD) detector (wavelength: 785 nm). The incident laser power was kept at 1 mW and total accumulation times of 10 s were employed.

## Results and discussion

We have previously shown that acid dopant can change the chemical nature and surface property of the conducting polymers, which leads to variation in morphology and size of the chemically deposited MNPs.<sup>14,17</sup> However, direct immersion of citric acid doped PANI membranes in AgNO<sub>3</sub> aqueous solutions only produce scattered Ag nanostructures with poor surface coverage. It is found that chemical deposition of Ag by PANI in AgNO<sub>3</sub> solutions with concentrations lower than 25 mM only results in Ag nanoparticles without any assembled structures (see Fig. S1 in ESI†). Fig. 1 displays the time-dependent structure evolution of the Ag microspheres by immersing the PANI membranes in 50 mM AgNO<sub>3</sub> aqueous solution. It is obvious that the nucleation and growth of Ag through chemical reduction of Ag<sup>+</sup> by PANI follows a very fast process. In 1 min, Ag microspheres with an average diameter of about 1  $\mu\text{m}$  are visualized on the PANI membrane (Fig. 1a). Of interest is that the



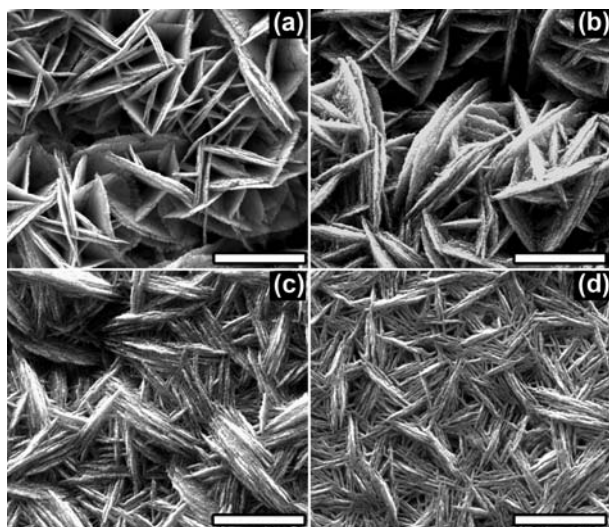
**Fig. 1** SEM images of silver nanostructures produced by immersing the PANI membranes doped by citric acid in 50 mM AgNO<sub>3</sub> solution for (a) 1 min, (b) 5 min, (c) 10 min and (d) 30 min. Scale bar: 2  $\mu\text{m}$ .

surface of the Ag microsphere is not smooth, but rough with sheet-like fine structures (inset in Fig. 1a). This sheet-like growth has been proven to be the intrinsic property of citric acid doped PANI membranes.<sup>17,21</sup> The growth of adjacent Ag nucleates can lead to interconnected Ag microspheres, however we still can see bare PANI uncovered by Ag. The sheet-like structures become distinct after the citric acid doped PANI membrane was immersed in 50 mM AgNO<sub>3</sub> for more than 5 min (Fig. 1b and c), with a slight increase in the diameter of those Ag microspheres. After 30 min, we can see Ag yarn-balls grown on citric acid doped PANI membranes, which are actually comprised of an ensemble of Ag nanosheets with thicknesses of about 20 nm (Fig. 1d). A careful observation reveals that those nanosheets are not smooth sheets, but single layers of assembled Ag nanoparticles (inset in Fig. 1d). Notably, as we even increase the reaction time, the surface of the PANI membrane cannot be fully covered by the Ag structures, which may result from the inhomogeneity of the membrane surface. The obtained structures are determined to be elemental Ag but not silver salts by EDAX and XRD studies (see Fig. S2 in ESI†). As we have shown, the bare PANI uncovered by metal structures can lead to tremendously reduced SERS responses, usually with an average enhancement factor of 10<sup>4</sup>–10<sup>5</sup>, which is almost two orders of magnitude weaker than that from the well-defined 3D Ag nanosheet structures on Au-supported PANI membranes.<sup>21</sup> It may be rationalized by the fact that those highly close packed Ag microspheres with limited surface areas will decrease the number of analyte molecules attached to the Ag surfaces.

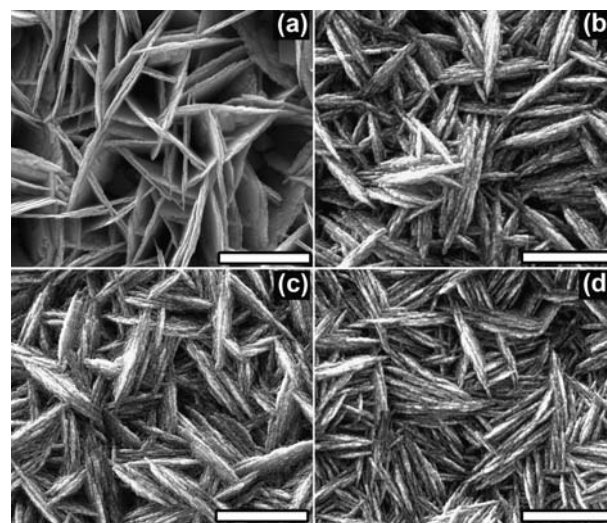
It is interesting to find that with a small amount of PANI (5 wt%) substituted by multi-walled carbon nanotubes (CNTs), which are more electrically conductive than doped PANI, the chemically deposited Ag structures completely cover the P-CNTs membrane surfaces (even in AgNO<sub>3</sub> aqueous solution with a concentration lower than 25 mM), without any bare PANI visible. Fig. 2 shows the Ag structures grown on citric acid doped P-CNTs membranes in AgNO<sub>3</sub> aqueous solutions with different concentrations. One can find that Ag nanosheets are not

assembled into close packed microspheres as seen on PANI membranes, instead, they are evenly distributed on P-CNTs membranes. We believe that the CNTs with higher electrical conductivity dispersed in the membranes act as electrical connectors for the PANI particles, and thus the electron transfer from PANI to Ag<sup>+</sup> can be facilitated, which creates a homogeneous nucleation environment for the Ag<sup>+</sup> over the whole surface of the P-CNTs membranes. With more nucleation sites, the growth of Ag still follows nanosheet growth, but no close packed microspheres are produced. It can also be seen that the build-up type of those Ag nanosheets are very sensitive to the concentration of AgNO<sub>3</sub> aqueous solutions. With the increase in AgNO<sub>3</sub> concentration, the Ag nanosheet assemblies are more closely stacked together, and the stereoscopic space between the nanosheets are decreased. Using 15 mM AgNO<sub>3</sub> aqueous solution (Fig. 2a), the Ag nanosheets are loosely stacked into flower-like structures; However, closely packed Ag nanosheet networks can be found in 100 mM AgNO<sub>3</sub> aqueous solution (Fig. 2d).

In view of the high cost of CNTs and in order to further study the effect of conductive additive in chemical deposition of Ag based on conducting polymers, conductive graphite (G) was used in membrane fabrication to study the Ag growth on P-G membranes. As shown in Fig. 3, one can see that homogeneous Ag nanosheet assemblies are again obtained, which verifies our hypothesis that it is the conductive additive that renders a homogeneous nucleation environment over the whole surface of the conducting polymer membranes. Similar to those on P-CNTs membranes, the build-up type of the Ag nanosheets are also sensitive to the concentration of AgNO<sub>3</sub> aqueous solutions. Therefore, the pack density and assembly of the Ag nanosheets on P-CNTs and P-G membranes can be well manipulated simply by controlling the concentration of AgNO<sub>3</sub> aqueous solution. With CNTs substituted by graphite, the cost of the conducting polymer membrane fabrication can be greatly reduced. Here, the Ag nanosheets with different pack densities offers a great opportunity to study the SERS responses from those various Ag structures.



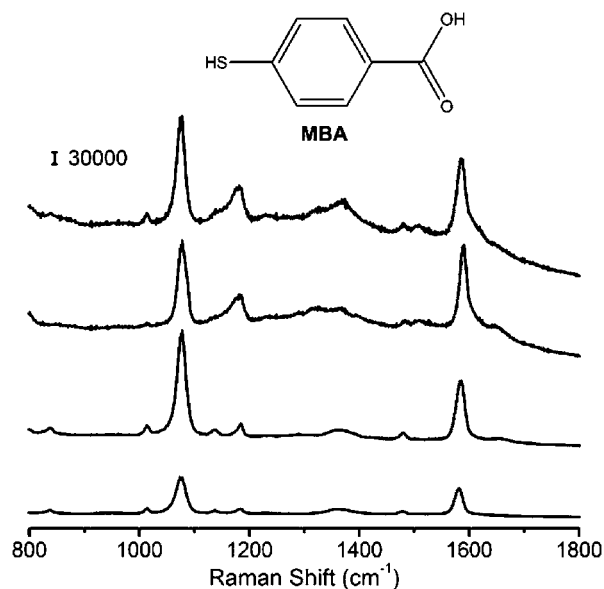
**Fig. 2** SEM images of silver nanostructures produced by immersing the P-CNTs membranes doped by citric acid in (a) 15, (b) 25, (c) 50 and (d) 100 mM AgNO<sub>3</sub> solution for 30 min. Scale bar: 1 μm.



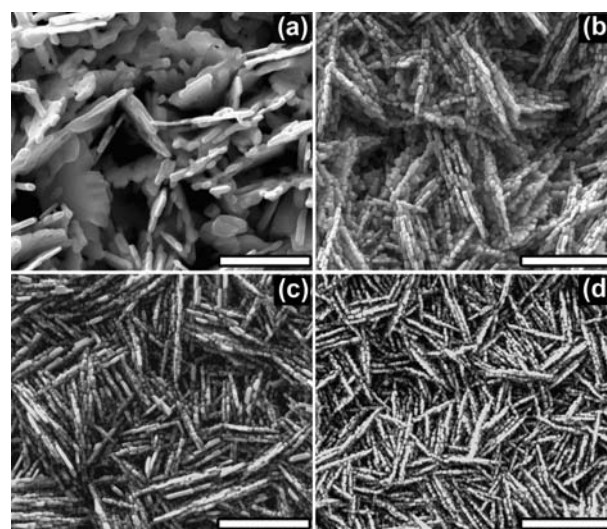
**Fig. 3** SEM images of silver nanostructures produced by immersing the P-G membranes doped by citric acid in (a) 15, (b) 25, (c) 50 and (d) 100 mM AgNO<sub>3</sub> solution for 30 min. Scale bar: 1 μm.

SERS activity of the Ag structures were taken on a 785 nm Raman apparatus in backscatter configuration by immersing the Ag-supported P-G substrates in a 4 mM mercaptobenzoic acid (MBA) ethanol solution for 15 min. Fig. 4 shows the SERS spectra of MBA adsorbed on Ag structures from P-G membranes. The SERS spectrum of MBA is dominated by the  $\nu_{8a}$  ( $\sim 1590\text{ cm}^{-1}$ ) and  $\nu_{12}$  ( $\sim 1080\text{ cm}^{-1}$ ) aromatic ring vibrations; other weak bands at  $\sim 1150$  and  $\sim 1180\text{ cm}^{-1}$  are attributed to the C-H deformation modes.<sup>22–24</sup> MBA, with a thiol group on one end and a carboxylic acid on the other end, has strong chemical interactions with Ag surfaces, however, the strong covalent bond between MBA and Ag does not lead to strong electronic coupling with the surface plasmon;<sup>25</sup> therefore, the SERS response mainly results from an electromagnetic enhancement which is common in metal structures with sharp edges, intersections and bifurcations, where nanoscaled roughness creates high local fields.<sup>26,27</sup> The close packed Ag nanosheet structure in Fig. 3(d) brings relatively weaker SERS signals, which may result from smaller surface areas available for the analyte binding. Strong signal enhancement ( $10^6$ – $10^7$ ) was discovered for those Ag-supported conducting polymer substrates, and the detection sensitivity can reach 5 ppm on those well-defined structures.

Etching has been proven to be an effective way to finely tune or transform the morphology and size of the prepared nanoparticles.<sup>28–31</sup> In our experiment, the Ag-supported P-G membranes as shown in Fig. 3 were immersed in 0.1 M HNO<sub>3</sub> for 15 min, which undergoes a corrosion reaction as:<sup>29</sup>  $3\text{Ag} + 4\text{HNO}_3 \rightarrow 3\text{AgNO}_3 + \text{NO} + 2\text{H}_2\text{O}$ . It can be seen in Fig. 5 that the fine structures of the nanosheets on P-G membranes are obviously changed, with the nanoparticles that assemble into nanosheets clearly visible by bare eyes. Of note is that prolonged immersion of those Ag-supported P-G membranes in HNO<sub>3</sub> aqueous solution will destroy those well-defined Ag structures and lead to bare PANI uncovered again (see Fig. S3 in ESI†). Therefore, this acid etching should be controlled carefully to



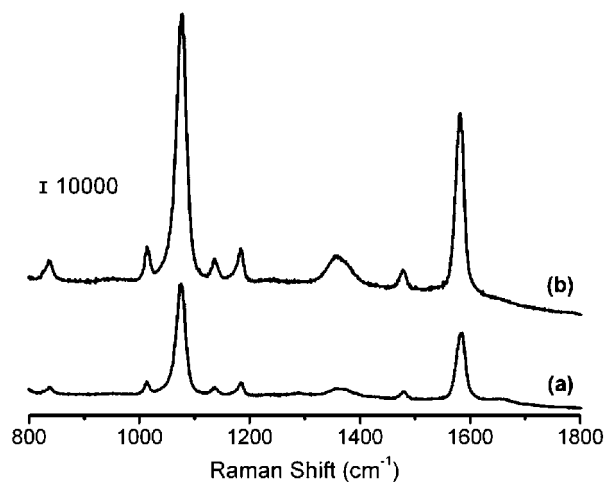
**Fig. 4** SERS spectra of mercaptobenzoic acid (MBA) adsorbed on silver nanostructures supported on P-G membranes. (a)–(d) correspond to the silver nanostructures as shown in Fig. 3.



**Fig. 5** SEM images of silver nanostructures produced by immersing the silver supported P-G membranes in 0.1 M HNO<sub>3</sub> aqueous solution for 15 min. (a)–(d) correspond to the silver nanostructures as shown in Fig. 3. Scale bar: 1  $\mu\text{m}$ .

maintain the homogeneous Ag structures on the conducting polymer membranes.

It is determined that proper acid etching of those Ag structures does bring enhanced SERS responses. Taking the sample with relatively lower SERS activity (shown Fig. 3d) for example, it can be seen that the SERS signal from the acid etched Ag structures can be normally 4–5 times stronger than that from the untreated one (Fig. 6). As we see from the etched samples, there is no doubt that proper acid etching creates higher surface areas and uniform surface roughness of those Ag structures. The exposed nanoparticles after acid etching, but not close packed ones that form the nanosheet, may be more favorable for molecule binding. Moreover, we believe the gaps between two exposed nanoparticles can present similar strong SERS enhancement as found in metal dimers.<sup>32,33</sup> The fact that proper acid etching of the Ag



**Fig. 6** A comparison of SERS responses of mercaptobenzoic acid (MBA) on silver nanostructures supported on P-G membranes before (a) and after (b) acid etching, which correspond to silver structures as shown in Fig. 3(d) and Fig. 5(d) respectively.

structures on the conducting polymer membranes leads to better SERS responses is also confirmed on other Ag structures.

## Conclusions

In summary, with a small amount of polyaniline (PANI) substituted by conducting additives (graphite or multi-walled carbon nanotubes) in the conducting polymer membranes, homogeneous Ag nanosheet assemblies that completely cover the membrane surfaces can be obtained. It is believed that the addition of conducting additives with higher electrical conductivities creates a homogeneous nucleation environment on the surface when Ag<sup>+</sup> ions were chemically reduced by PANI. The prepared well-defined Ag nanosheet hierarchical structures show strong SERS responses toward the analyte molecule, with a detection sensitivity down to 5 ppm. With a controlled acid etching in dilute HNO<sub>3</sub> aqueous solution, the obtained Ag nanostructures with more exposed nanoparticles and higher surface areas can have 4–5 times stronger Raman enhancement than the untreated samples. Compared with the commercially available silicon-based SERS substrates, we think the as-prepared homogeneous Ag nanosheet assemblies fabricated on conducting polymer membranes can be more cost-effective and attractive in SERS detection of chemical or biological molecules.

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