

Silver Porous Nanotube Built Three-Dimensional Films with Structural Tunability Based on the Nanofiber Template-Plasma Etching Strategy

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A facile and high-throughput strategy is presented to fabricate three-dimensional (3D) hierarchically porous Ag films, with clean surfaces, via plasma etching Ag-coated electrospun nanofiber template. The films are built of Ag porous nanotubes and are homogeneous in macro-size but rough and porous in nanoscale. Each nanotube-block is micro/nanostructured with evenly distributed nanopores on the tube walls. The film architecture (or the shape, arrangement, and distribution density of porous nanotubes; the number and size of nanopores) can be easily controlled by the nanofiber-template configuration, Ag coating, and plasma etching conditions. Such hierarchically porous films could be very useful, such as in catalysis, sensors, and nanodevices. They have exhibited significantly structurally enhanced surface-enhanced Raman scattering performance with good stability and reproduction, and shown the possibility of molecule-level detection. Also, the strategy is universal for fabricating other hierarchically structured 3D metal porous films, such as porous Ag hollow sphere arrays.

1. Introduction

Three-dimensional (3D) Ag nanostructured porous films have received considerable attention recently due to their outstanding properties and potential applications in catalysis,¹ superhydrophobicity,² lithium ion batteries,³ and so forth. Especially, they are excellent substrates for surface-enhanced Raman scattering (SERS) sensors due to their high density of hot spots and hence significant enhancement ability and large surface area to adsorb detected molecules.^{4–6} Several fabrication methods have been developed, including electrodeposition,⁷ electrophoresis,⁸ chemical reduction,⁹ selective etching,¹⁰ thermal decomposition,¹¹ template routes (polyethyleneimine hydrogel¹² and colloidal crystal²), and so forth. However, it is still a challenge to control the architecture of films, tune the size of nanopores, and obtain contaminant-free surfaces, which are important for practical applications. A promising way to overcome these issues is to build 3D structured films, according to needs, by the micro/nanostructured porous blocks with tunable structures and clean surface (such as tubes, hollow spheres, etc.). Such porous block built 3D films would be controllable and tunable in structure and hence in practical performance. To our knowledge, however, there is no report on fabrication of such films.

Here we present a flexible and simple way to build the 3D Ag porous films with controllable and tunable structures based on a nanofiber template/plasma etching strategy, as schematically shown in Figure 1. First, the electrospun polystyrene nanofibers (PNs) were coated with Ag by ion beam sputtering and subsequently removed by dissolution. The Ag tubes were thus left. Then, plasma etching was performed on the Ag tube-packed films, and finally the 3D structured Ag porous films with clean surface were thus obtained. The films are contaminant-free, built of Ag porous nanotubes, and homogeneous in macro-size but rough and porous in nanoscale. Each nanotube-block is micro/nanostructured with evenly distributed nanopores on the tube walls. The film architecture (or the arrangement and distribution density of porous nanotubes; the number and size of nanopores) can be easily controlled by the nanofiber-template configuration and plasma etching conditions. Such hierarchically porous films could be very useful, such as in catalysis, sensors, and nanodevices. They have exhibited significantly structurally enhanced SERS performance and shown the possibility of molecule-level detection. Also, this strategy is universal for fabricating other hierarchically structured 3D metal porous films, such as porous Ag hollow sphere arrays. The details are reported in this Letter.

2. Experimental Section

2.1. Preparation of Polystyrene Nanofibers. Polystyrene (homopolymer, MW = 220 000, Beijing Yanshan Petrochemical Co., Ltd.) was dissolved in dimethylformamide (Yongzhou Hubao Fine Chemical Co.) by stirring for 6 h to form a 25 wt % transparent solution. About 4 mL of such solution was placed in a 5 mL syringe equipped with a blunt metal needle of 0.7 mm in hole diameter. The syringe was placed in a syringe pump that maintained a solution feed rate of 0.5 mL/h. A stainless steel drum covered with a sheet of aluminum (Al) foil was employed as the collector. The rotation speed of the drum was fixed at about 200 rps. The distance between the needle tip and the collector was 25 cm, and the voltage was set at 20 kV. The final nanofiber packed film, with white color, was of several centimeters in size and about 20 μm in thickness.

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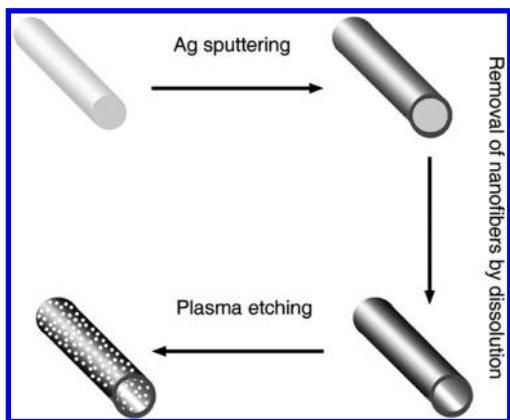


Figure 1. Schematic illustration of the strategy for fabrication of Ag porous nanotube.

2.2. Ag Coating. Silver was deposited or coated on the electrospun nanofiber films by using a commercial ion beam sputtering system at a pressure of 7.5×10^{-5} Torr (Shenyang City Keyou Institute of Vacuum Technology, China). Ar was used as shielding gas. Acceleration voltage was 1.2 kV, and ion current was 2.5 mA. The deposition rate was about 0.1 nm s^{-1} , and the coating thickness was controlled by sputtering time. After deposition, the inner PNs were removed by dissolution in CH_2Cl_2 solution with ultrasonic vibration. The Ag nanotube packed films were thus obtained. For reference, the continuous 2D Ag thin film was also prepared on Al foil without the PNs under the same sputtering conditions.

2.3. Plasma Etching and Characterization. The Ag nanotube packed films and the corresponding continuous 2D thin film were etched with radio frequency (RF)-excited Ar plasma in an argon plasma cleaner (PDC-32G-2, Harrick Plasma Co.) at a pressure of 0.15 Torr and an input power of 100 W for 40 min. The flow rate of Ar gas was 8 SCFH (standard cubic feet per hour).

The samples were examined by field-emission scanning electron microscopy (FESEM, Sirion 200). X-ray diffraction (XRD) measurements were conducted on a Philips X'Pert instrument with Cu $K\alpha$ radiation. The size distributions were acquired by measurement of more than 100 in count from FESEM images using Photoshop software.

For SERS spectral examination, the samples were first dipped into a solution with 10^{-9} M rhodamine 6G (R6G) for 3 h, rinsed with deionized water to remove unbound R6G molecules, and dried in the air. Raman spectral measurements were conducted on a French LABRAM-HR confocal laser microRaman spectrometer with an air-cooled Ar ion laser at 514.5 nm and a laser beam spot $5 \mu\text{m}$. Laser power was 10 mW.

3. Results and Discussion

Figure 2a shows a typical morphology of PNs by electrospinning, which are randomly arranged and form a loose-fiber film. The PNs are of 300 nm mean diameter and narrow size dispersion. After Ag coating by ion beam sputtering on the PNs and removal of them, we can obtain a homogeneous film with several centimeters in scale on Al foil, as shown in the inset of Figure 2a (a photo of the film). XRD shows that the obtained film is Ag with fcc structure (Supporting Information Figure S1). Typically, Figure 2b shows the morphology corresponding to the product after Ag sputtering for 7 min (about 40 nm in the coating thickness) and removal of PNs. Obviously, compared with the original PNs, these fibers, which are composed of nanoparticles with tens of nanometers in size, become bigger in diameter due to the coated Ag shells. However, they are still well isolated from each other and keep fibrous morphology. A cross-sectional view

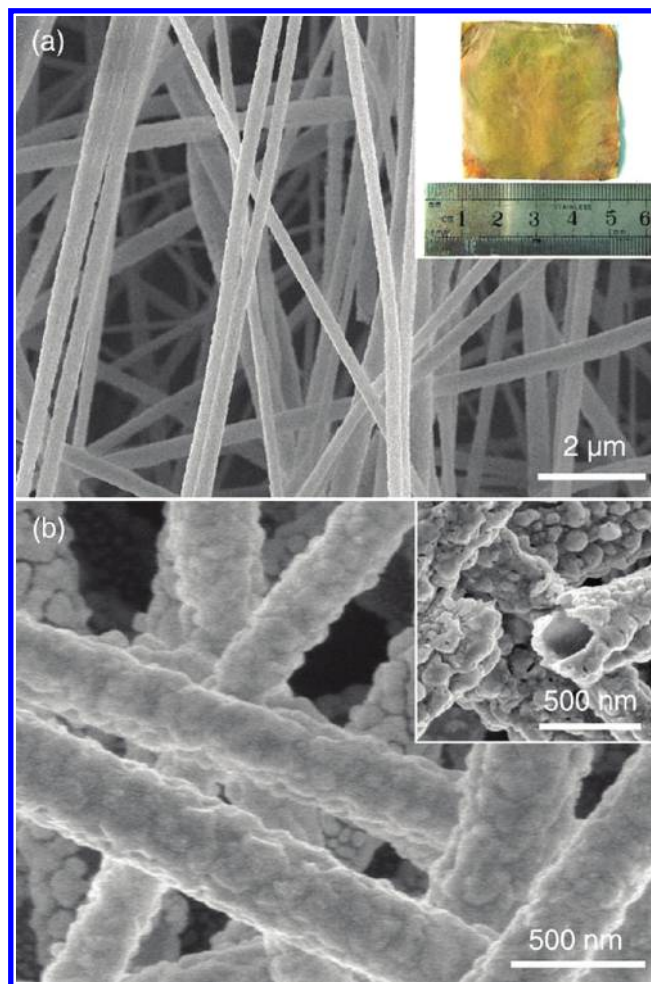


Figure 2. FESEM images of electrospun polystyrene nanofiber film before (a) and after Ag coating (7 min Ag sputtering) and subsequent removal of the nanofibers (b). Inset in (a): photo corresponding to (b). Inset in (b): cross-sectional view of a single tube (about 40 nm in thickness).

reveals that the Ag fibers are tubularly structured, as shown in the inset of Figure 2b, due to ion sputtering induced nonshadow deposition.¹³ Supporting Information Figure S2 gives a FESEM image in the edge region of the sample, showing more fibrous end parts with tubular structure.

It should be pointed out that the Ag shell near top part of the film is slightly thicker than that at the lower part due to different accessibility of the sputtered Ag atoms/clusters to different places. Under our conditions, the sputtering deposition of Ag (7 min Ag sputtering) can be relatively homogeneous for the tube-built film within $10 \mu\text{m}$ in thickness. The film thickness can be controlled by the electrospinning duration. However, if the loose PN template (film) is too thick (say, $> 20 \mu\text{m}$ in thickness), the Ag coating on the PNs at the lowest position of the film could be discontinuous. These discontinuous coatings could be removed during subsequent removal of PNs by ultrasonic vibration, and thus, the final nanotube-built film would be thinner than the original one.

3.1. Morphologies and Structure. After Ar plasma etching on the Ag nanotube-built film for about 40 min, numerous nanopores are formed on tube walls, as shown in Figure 3. The sample is uniform over the centimeter scale due to isotropic plasma bombardment on the Ag nanotubes. However, all the nanotubes

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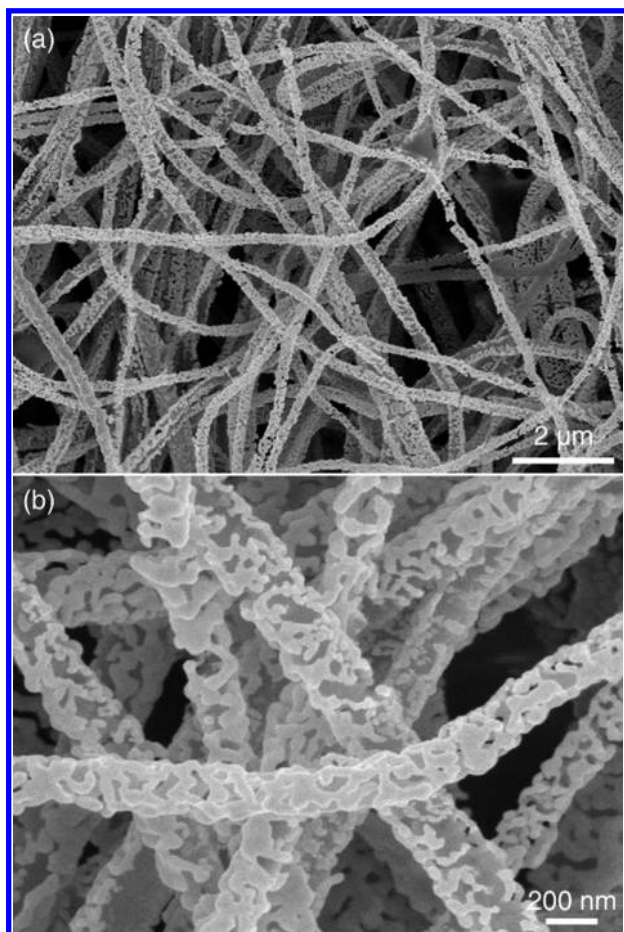


Figure 3. FESEM images of the sample, shown in Figure 2b, after 40 min plasma etching (at different magnifications).

retain fibrous profile without distortion. The nanopores are penetrating through the tube walls and irregular in shape and are nanometers to tens of nanometers in scale. As a whole, such Ag porous nanotubes are micro/nanostructured, and the constructed 3D film is homogeneous in macroscale but hierarchically rough and porous in micro/nanoscale. In addition, this film should be contaminant-free due to the plasma bombardment during preparation. The corresponding energy-dispersive X-ray spectroscopy (EDX) analysis has been done for such porous nanotube-built 3D films, as shown in Supporting Information Figure S3. There are only the peaks for Ag and Al (herein, Al signal is from the Al substrate), demonstrating the clean surface. Hence, the plasma etching is an effective technique for surface micromachining of Ag 3D nanostructured porous films with a clean surface. Importantly, the film is free-standing and flexible, and it can be tailored freely or transferred to the other substrates (see Supporting Information Figure S4, corresponding to that being transferred on an ITO substrate from the Al foil). We can thus obtain a homogeneous Ag porous nanotube-built film, with much higher than 20 μm in thickness, by putting two or more pieces of thin homogeneous films together.

3.2. Structural Tunability. Further experiments have revealed that the film architecture is tunable by the PN template configuration, Ag sputtering time, and plasma etching conditions.

The arrangement and distribution density of the porous nanotubes can be easily controlled by the electrospinning-induced PN-template's configuration. Supporting Information Figure S5 shows the film consisting of the aligned porous nanotubes, from the aligned PNs. Supporting Information Figure S6 exhibits the

morphologies of the films with different distributed densities of porous nanotubes, from PN templates with different electrospinning durations. Also, the size of nanotubes can be tuned by electrospun PNs and/or subsequent plasma etching.¹⁴ The easy control of the structural polymorphism is important in practical applications.

Further, the pore shape in the porous tubes strongly depends on the Ag sputtering time. With increasing sputtering time, tube wall increases in thickness. Typically, Figure 4 shows the results corresponding to 5 and 30 min Ag sputtering (the other experimental conditions are the same as those of the sample in Figure 3). For the former, the film is packed by the broken Ag nanotubes (Figure 4a), which consist of smaller nanoparticles (20–80 nm in size), and exhibits a nanoparticle-aggregated structure, as shown in Figure 4b and its inset. For the latter, it is built by the integrated nanotubes, with uneven but smooth surfaces as well as homogeneously distributed nanoholes (10–45 nm in size), and the nanoholes are formed at the cupped sites on the tube surface (Figure 4c, d and the inset).

In addition, the number and size of nanopores are variable by altering plasma etching times. Shorter etching corresponds to less and smaller nanopores, or vice versa. Supporting Information Figure S7 shows the typical results after different etching times for the sample with 30 min Ag sputtering deposition. When the etching is short (say, 10 min), only few shallow nanopits on the surface of nanotubes are observed (Supporting Information Figure S7b). After etching for enough time (say, > 20 min), a large number of nanopits together with nanopores are formed (Supporting Information Figure S7c and Figure 4c).

3.3. Formation of Nanopores on Tube Walls. The plasma bombardment formation of nanopores on tube walls is easily understood. Ag, unlike other metals, has a high surface mobility, even at room temperature.¹⁵ During plasma etching, the Ar^+ bombardment will induce densification and even surface melting (or sputtering) of the deposited Ag shells, due to the energy transferring. For the sample with thick coating, such densification will result in contraction of the Ag shells and hence formation of nanoholes or nanopits on the cupped sites, as shown in Figure 4c. Also, the surface melting leads to a smooth surface (see Figure 4d). For the sample with thin coating, which is of lower heat capacity, the tubular morphology will be destroyed due to the sputtering induced etching (see Figure 4a).

3.4. Universality of the Strategy. It should be mentioned that the strategy presented in this study can be extended to fabricate the other hierarchically 3D structured Ag porous films based on some frequently used templates, such as the polystyrene sphere template.¹³ Supporting Information Figure S8 shows the porous Ag hollow sphere-built arrays using the Ag-coated monolayer polystyrene sphere array, after the same experimental processes as those in Figures 3 and 4. We can see the similar block surface morphology.

3.5. Strong SERS Activity. Such hierarchically porous Ag 3D films have great potential for practical applications in many fields, such as catalysis, sensors, and nanodevices. Here we only present the SERS performance of such films to demonstrate their structural advantage, by taking the sample shown in Figure 3 as an example. It has been found that this porous film exhibits a significantly structurally enhanced SERS effect using R6G as the probe molecule, as shown in curve 1 of Figure 5a. For comparison, the original sample without plasma etching shown in Figure 2b

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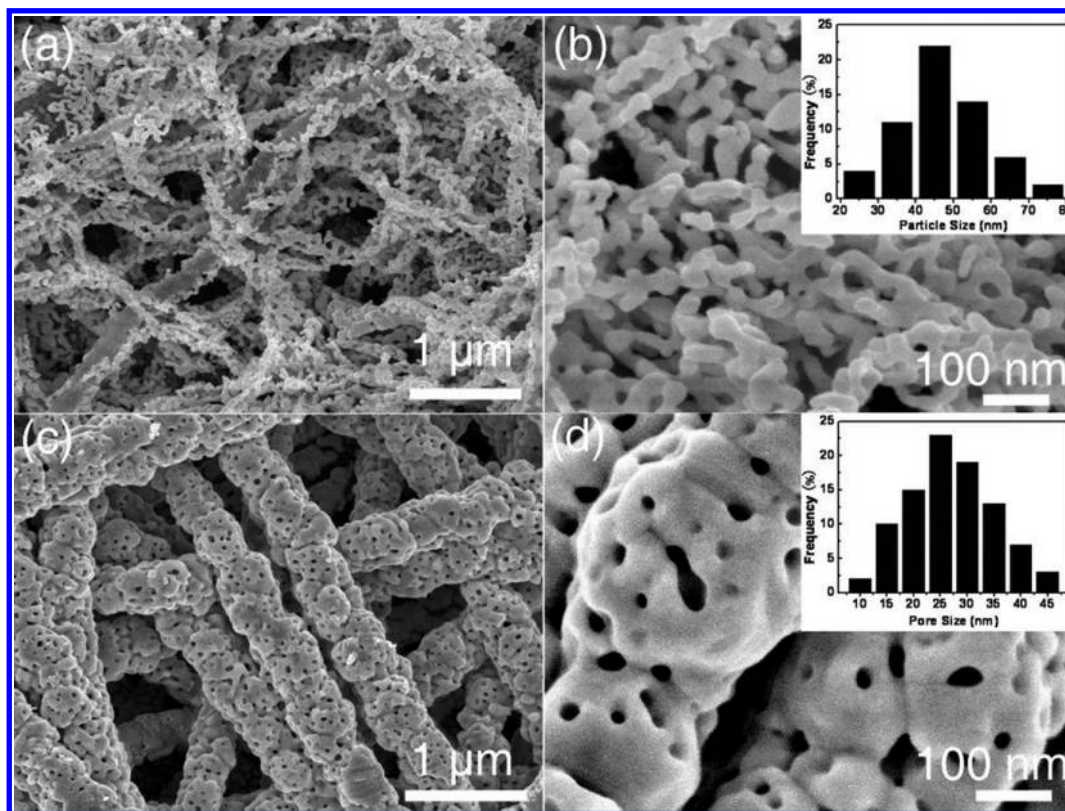


Figure 4. Morphologies of the films corresponding to the Ag coating with different thicknesses and 40 min plasma etching. (a, b) 5 min Ag sputtering (at different magnifications). Inset in (b): particle size distribution. (c, d) 30 min Ag sputtering (at different magnifications). Inset in (d): pore size distribution.

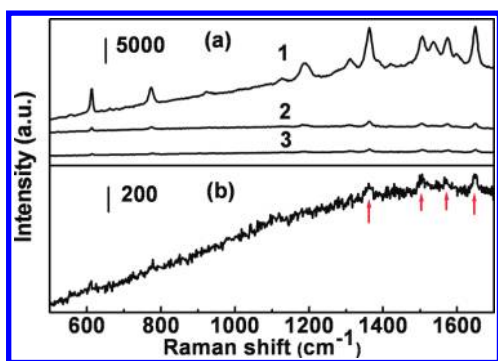


Figure 5. Raman spectra of R6G molecules on different substrates. (a) 10^{-9} M R6G, data integration time = 5 s. Curve 1: hierarchically porous Ag 3D film shown in Figure 3. Curve 2: sample shown in Figure 2b (without plasma etching). Curve 3: 2D Ag porous film (without using PNs, or shown in Supporting Information Figure S7). (b) 10^{-14} M R6G, data integration time = 15 s. Curve in (b): hierarchically porous Ag 3D film shown in Figure 3. [The arrows in (b) show the peaks in the range above 1300 cm^{-1} .]

and the corresponding 2D Ag film obtained by plasma etching (Supporting Information Figure S9) were also measured under the same experimental conditions. Obviously, the SERS signal from the hierarchically porous film is significantly enhanced compared with the original film (curve 2). Only a very weak signal was detected for the 2D porous film (curve 3). For the hierarchically porous film, the minimum detectable concentration of R6G can be down to 10^{-14} M when using a short data integration (15s) (Figure 5b), which shows the possibility of molecule-level detection. Correspondingly, for the original sample without plasma etching and the 2D porous film, there are no

detectable signals. Further, it has been revealed that the hierarchically porous film is of good stability and reproduction in SERS signal, and there is no observable loss of SERS activity at least for one month in our experimental condition.

Compared with the film without plasma etching, we can know that the nanopores on the Ag tube walls play a dominant role in the enhanced SERS. The strong SERS effect for the hierarchically porous film should be attributed to its unique structure: allowing efficient coupling among the nanoscaled interstitials, including inside and between Ag porous nanotubes, and possessing more surface area exposing to environment, compared with two other substrates.^{6,8,16} Upon optical excitation, the hot spots, especially the hottest ones, support extremely intense local electromagnetic fields and thus bring strong Raman signal of the local adsorbed probe molecules.^{6,17} Furthermore, it should be mentioned that the 3D hierarchically porous film in this study has four advantages: (1) The long and interconnected fibrous structure avoids coagulation of nanoparticles (one vital drawback for some nanoparticles' films), making them stable. (2) Plasma etching can remove organic contamination (polystyrene and/or CH_2Cl_2 , if any) during the fabrication process, and the fresh surfaces of Ag nanoparticles are thus retained, which are important advantages for keeping high SERS activity and adsorbing detected molecules. (3) The crossing geometry of nanotubes minimizes the polarization dependence of the exciting laser, since half of them always possess the largest enhancement (in the optimal spacings between nanoparticles and between nanotubes) from a viewpoint of statistics. The trade-off makes the film a perfect substrate like the randomly stacked dielectric/metal composite nanowires as previously

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reported.¹⁸ (4) The film structure is tunable, by multiparameters, for further SERS optimization.

4. Conclusions

In summary, a facile and high-throughput strategy is presented to fabricate the 3D hierarchically porous Ag films with clean surface via plasma etching Ag-coated electrospun nanofiber template. The films are built of Ag porous nanotubes and are homogeneous in macro-size but rough and porous in nanoscale. Each nanotube-block is micro/nanostructured with evenly distributed nanopores on the tube walls due to isotropic Ar⁺ bombardment and etching. The film architecture can be easily controlled by the template configuration, Ag sputtering time, and plasma etching conditions. Further, the film is flexible and can be transferred to any other substrates. Importantly, due to its unique 3D structure

and clean surface, such a hierarchically porous film has exhibited strong SERS activity with good stability and reproduction, and it shows the possibility of molecule-level detection. It should have also great potential for practical applications in catalysis, sensors, and future nanodevices. The strategy presented in this work is inexpensive, large-scale, and easy to control. It is also universal for fabrication of other hierarchically structured 3D metal porous films, such as porous Ag hollow sphere arrays, based on some frequently used templates.

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Supporting Information Available: XRD and EDX spectra, and FESEM images for some samples. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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