Electronic Supporting Information

Mesoporous poly(ethylene-*co*-vinyl alcohol) monolith captured with silver nanoparticles as a SERS substrate: facile fabrication and ultra-high sensitivity

Guowei Wang,[a] Hiroyuki Yoshikawa,[b] Eiichi Tamiya,[b] and Hiroshi Uyama*[a]

[a] Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

*Corresponding author E-mail: uyama@chem.eng.osaka-u.ac.jp;

Fax: +81-6-6879-7367; Tel: +81-6-6879-7364

[b] Department of Applied Physics, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

Fax: +81-6-6879-7840; Tel: +81-6-6879-7839

S1. Experimental section

1.1. Materials

Poly(ethylene-*co*-vinyl alcohol) (EVOH) with ethylene content of 27 mol % was supplied from Sigma. The number average molecular weight and weight average molecular weight measured by SEC were 6.8×10^4 and 1.6×10^5, respectively. 4-Mercaptobenzoic acid (MBA), rhodamine 6G (R6G), ethanol, isopropanol (IPA), acetone and silver nitrate were purchased from Wako Co. All reagents were used as received without further purification.

1.2. Instrumentation

Scanning electron microscope (SEM) observations were carried by using Hitachi Co., SU3500 at an accelerating voltage of 15 kV. Before observations, the monolith was pretreated by sputtering with pure gold in vacuo. The nitrogen adsorption/desorption isotherms of the AgNPs-EVOH monoliths were measured by using a NOVA-4200e surface area & pore size analyzer (Quantachrome Instruments) at 77 K. Energy dispersive X-ray spectrometric (EDX) result was obtained by utilizing Hitachi Miniscope TM3000 with a Swift 3000 equipment. Transmission electron microcopy (TEM) images of the monolith were recorded in a Hitachi H-7650 TEM.

For Raman imaging, fragments of AgNPs -EVOH monoliths were put onto a glass plate. They were mounted onto the sample stage of Zeiss inverted optical microscope (Axiovert 200), subsequently. A diode-pumped solid-state (DPSS) laser beam (Photop Suwtech, DPGL-2100) with a wavelength of 532 nm was focused using a 10x objective lens onto a monolith fragment. The intensity of laser beam through the objective lens was 2 mW. The Raman spectra were detected by a spectrometer consisting of a polychromator (Andor, SR-303i) and a charge-coupled device (CCD) camera (Andor, DU970P-BV). In order to block the excitation laser beam, a long-pass edge filter (Semlock, LP03-532RU) was placed in the optical path to the spectrometer. Each Raman spectrum was obtained for 10 sec in the spectral range of 100-3700 cm^{-1}.

1.3. Preparation of AgNPs-EVOH monoliths

A typical procedure for the preparation of a AgNPs-EVOH monolith was as follows. EVOH (300 mg) was dissolved in a mixed solvent of IPA (1.3 mL) and water (0.7 mL) at 75 ^{o}C to prepare the EVOH solution. Two hundred mg of silver nitrate was added to the solution and stirred for 6 h. Then the solution was cooled at 4 ^{o}C to form the AgNPs-EVOH monolith. The embedded solvents were removed by immersing the monolith into acetone and subsequently the monolith was dried under vacuum.

1.4. SERS evaluations

AgNPs-EVOH monolith (20 mg) was immersed in 10 mL of R6G (10^{-6} M) ethanol solution for 2 h. Afterwards, the sample was washed by excessive amount of ethanol to remove unbounded R6G molecules, and the sample was dried in room temperature to remove ethanol. The sample was grinded to mesoporous EVOH powder for further SERS measurements.

In the case of MBA, a stock ethanol solution of MBA with the concentration of 10^{-3} M was prepared. This solution was diluted to give the MBA solutions of the appropriate concentration. AgNPs-EVOH monolith was treated by the solutions using a similar procedure as the case of R6G.

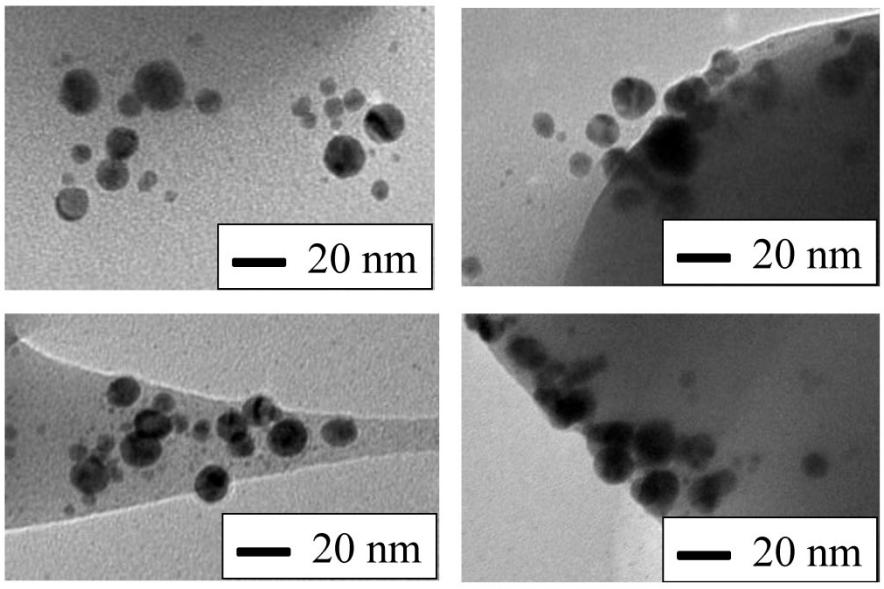

Figure S1. TEM images taken from the ultrathin fraction of the AgNPs-EVOH monolith

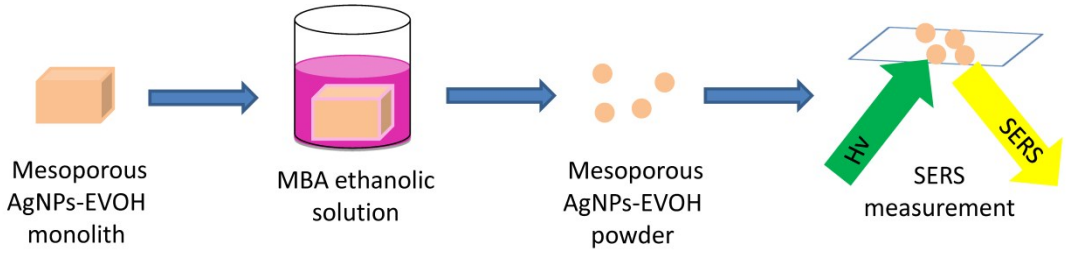

Figure S2. Illustration of the preparation of samples for SERS measurements.

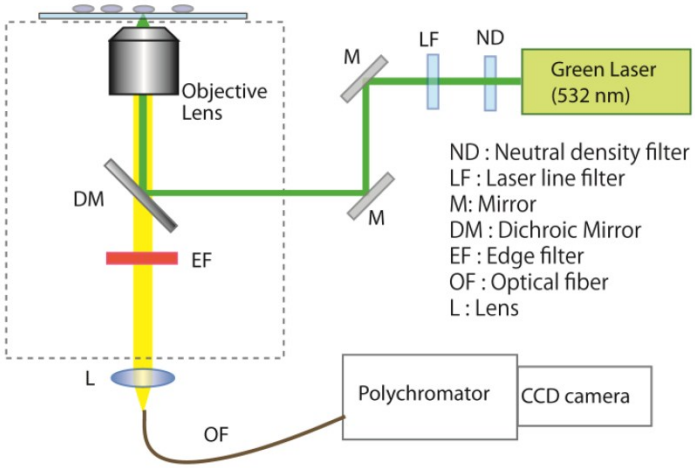

Figure S3. Illustration of the experimental setup for SERS measurements.

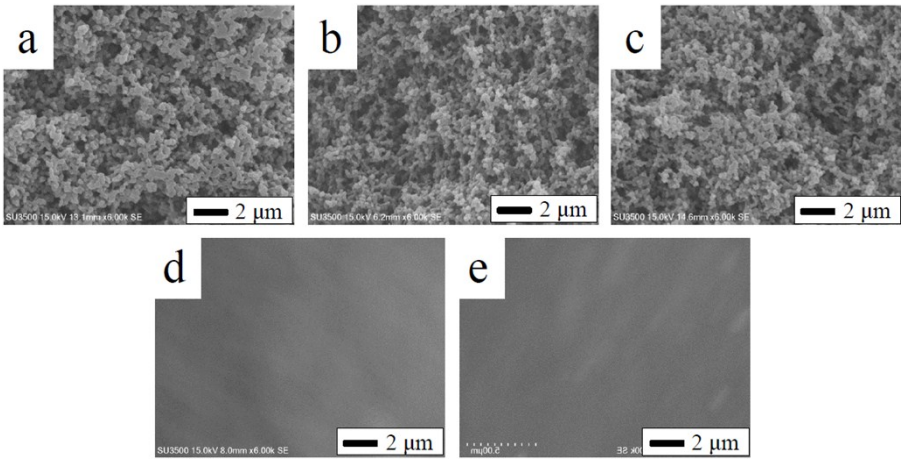

Figure S4. SEM images of the AgNPs-EVOH monoliths fabricated from different weight ratio of silver nitrate/EVOH: (a) 0.13, (b) 0.33, (c) 0.67, (d) 1.3, (e) 2.6.

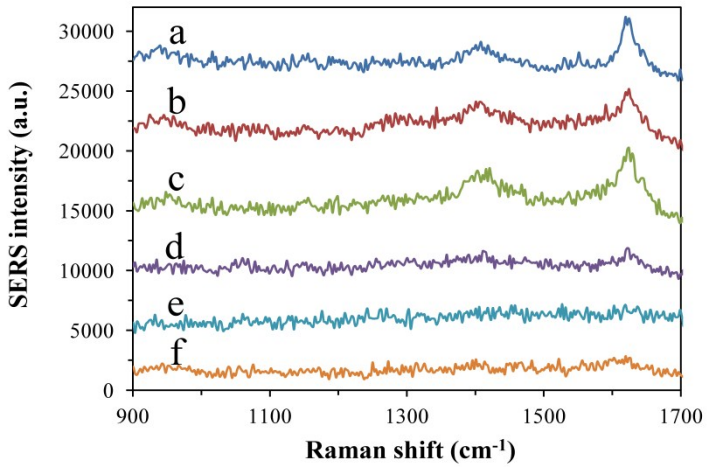

Figure S5. SERS spectra of 10^{-11} M of MBA adsorbed on AgNPs-EVOH monoliths fabricated from different weight ratio of silver nitrate/EVOH: (a) 0.13, (b) 0.33, (c) 0.67, (d) 1.4, (e) 2.8. SERS spectrum of pure AgNPs-EVOH monolith (silver nitrate/EVOH: 0.67 (w/w)) without MBA was used as reference (f).

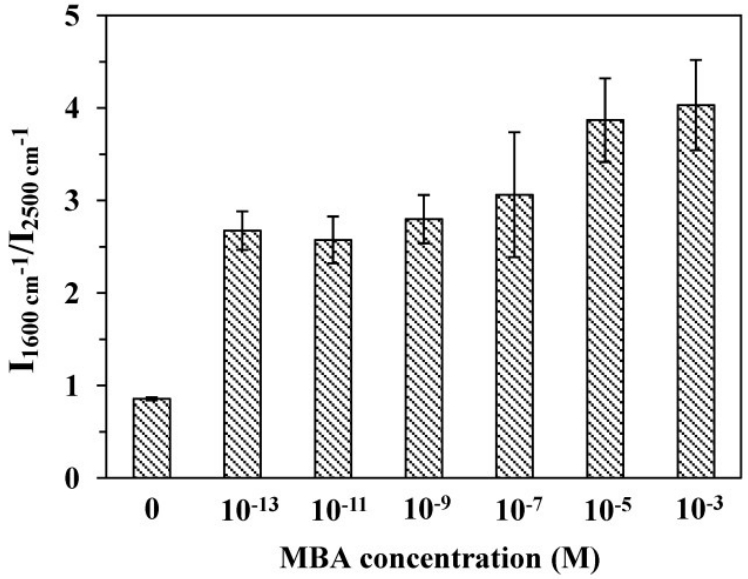

Figure S6. Intensity ratio of the peak at 1600 cm^{-1} and the peak at 2500 cm^{-1} with different MBA concentrations.