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Cite this: *RSC Adv.*, 2015, 5, 25777Received 6th January 2015
Accepted 5th March 2015

DOI: 10.1039/c5ra03585f

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

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A facile method to fabricate a mesoporous poly(ethylene-co-vinyl alcohol) (EVOH) monolith captured with silver nanoparticles (AgNPs) was developed. The formation of AgNPs and the monolith was in a one-pot process. The obtained monolith demonstrated ultrasensitive surface-enhanced Raman spectroscopy (SERS) responses.

SERS has attracted the interest of scientists as a powerful technique to detect chemical and biological molecules of trace concentration. The ultra-high sensitivity is due to the enhancement of the local electromagnetic field caused by nano-scale gaps (also called Raman “hot spots”) between metal nanostructures. Metal nanoparticles or nanostructures in types of roughed metal electrodes,^{1–3} metal nanoparticles colloids,^{4–6} metal nanoparticles-assembled planar substrates^{7,8} and metal nanoparticles-embedded three-dimensional (3-D) porous substrates⁹ have been developed as efficient SERS substrates. Among these SERS substrates, the 3-D porous ones are preferred because the open pores and the high surface area enable fast permeation and efficient adsorption of target analytes, respectively. In addition, the porous structure is considered to be able to improve the SERS performance on a large scale.¹⁰

So far, various 3-D porous SERS substrates have been prepared by immobilizing metal nanoparticles into a porous matrix such as porous gel,¹⁰ nanofiber,¹¹ porous alumina,⁹ porous silicon,¹² monolith,^{13,14} MOF¹⁵ and paper.¹⁶ For the construction of SERS substrates, a facile, cost-effective and largely-scalable method is highly demanded. However, the preparation of metal nanoparticles and a porous matrix is generally in separated processes, which is costly and somewhat

wearisome. Thus, it remains a great challenge for preparation of 3-D porous SERS substrates by a simply one-pot process.

Polymer monoliths with mesoporous structure have been developed in our group by a facile thermally induced phase separation (TIPS) method.^{17,18} Mesoporous polymer monoliths with open pores and large surface areas are especially useful for applications of 3-D porous SERS substrates. In order to get monolith-based 3-D SERS substrates with uniform mesopores, well dispersed metal nanoparticles and high SERS signal reproducibility, facile synthesis of a metal-polymer monolith using a one-pot process is indispensable and of particular interest.

In this study, we report a new and straightforward method to embed AgNPs into a mesoporous EVOH monolith (AgNPs-EVOH monolith). A simple one-pot process yielded AgNPs-EVOH monolith with uniform mesopores and well dispersed AgNPs. We further demonstrated that the monolith could be used as a SERS substrate with both ultrasensitive SERS responses and high SERS signal reproducibility. Our study enables the preparation of a 3-D porous SERS substrate with a facile method, which is as simple as other methods.^{19,20}

The general procedure for the fabrication of the mesoporous AgNPs-EVOH monolith is illustrated in Fig. 1. Silver nitrate was added to an EVOH solution of a mixed solvent of isopropanol (IPA) and water (IPA/water: 65/35 (v/v)) at 75 °C and the solution was gently stirred. The solution was cooled to 4 °C to form a monolith by TIPS. The resulting monolith was immersed into acetone to remove the embedded solvent and subsequently

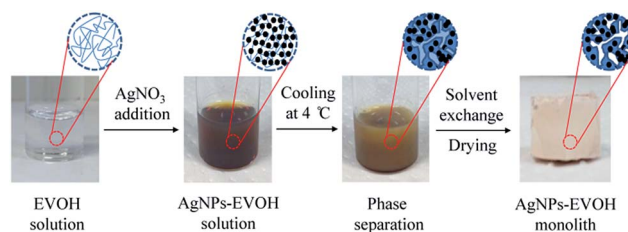


Fig. 1 A general procedure for fabrication of AgNPs-EVOH monolith.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra03585f



dried under vacuum. In this method, IPA acted both as a component of the mixed solvent to dissolve EVOH at the high temperature and as an agent for the reduction of the silver ion; the analysis of the solution after the monolith formation suggested that more than 97% of silver ion was reduced. EVOH was initially acted as a stabilizer to protect AgNPs from large scale aggregation and subsequently acted as a gelator to form the monolith with uniform mesopores. The present simple method to prepare the metal nanoparticles-embedded monolith is suitable for large scale production. Moreover, the monolith could be tailored into any desired shapes for the further SERS applications.

The nitrogen adsorption/desorption isotherms of the monolith exhibited a typical V isotherm with a relatively wide type H1 hysteresis loop in the P/P_0 range from 0.7–0.9, which is the characteristic of the mesoporous structure (Fig. 2). The formation of uniform mesopores centred at *ca.* 5.0 nm was proved by the pore size distribution (PSD) plot (insert), which was obtained by using the non-local density functional theory (NLDFT) method. The specific surface area was determined as $60.1 \text{ m}^2 \text{ g}^{-1}$ by multi-point BET method. These data indicate that the AgNPs–EVOH monolith had relative uniform mesopores and large specific surface area.

Fig. 3A shows a scanning electron microscope (SEM) image of the monolith. The SEM image clearly indicates the 3-D open macropore structure of the monolith. The existence of both mesopores and macropores enabled the capture of more target analytes and faster transport of these molecules to the surface of AgNPs. A transmission electron microscopy (TEM) image implies the existence of AgNPs with a typical diameter of 5–20 nm (Fig. 3B). It is interesting that most of the formed AgNPs were not spatially-isolated, but partially aggregated as silver dimers or clusters (Fig. S1†). Many researchers revealed that strong SERS signals often present at the junction of several nanoparticles.²¹ On the other hand, single nanoparticles often result in little enhancement. Thus, the formation of partially aggregated AgNPs made the monolith a potential SERS substrate with ultra sensitivity. The corresponding energy dispersive X-ray spectrometric (EDX) map (Fig. 3C) of the

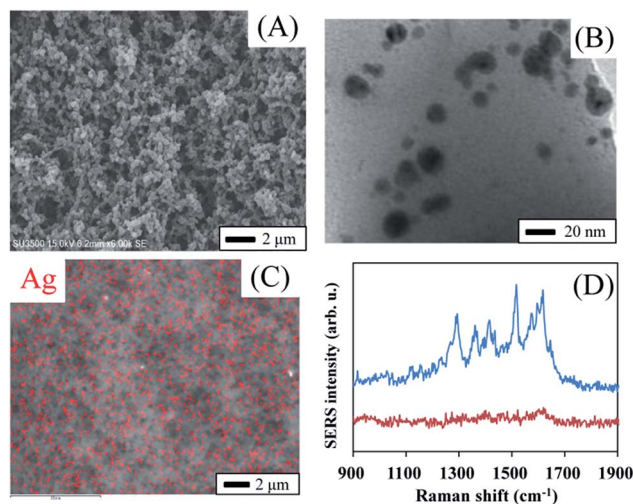


Fig. 3 SEM (A), TEM (B) and EDX (C) (red spots represent the existence of AgNPs) images of AgNPs–EVOH monolith. SERS spectrum (—) of R6G collected from the monolith and Raman spectrum (—) of the monolith (without R6G) (D).

monolith shows that the AgNPs were dispersed homogeneously in the 3-D porous monolith, although the EDX mapping was somewhat affected by the rough surface of the monolith. Fig. 3D demonstrates the SERS spectrum of rhodamine 6G (R6G) from the monolith that was treated with a R6G solution at concentration of 10^{-6} M . R6G showed characteristic SERS peaks, whereas the monolith exhibited clear background without any significant peaks in the Raman shift range from 900 cm^{-1} to 1900 cm^{-1} . All of these results indicate that the present monolith could be used as a good SERS substrate.

To evaluate the efficiency of the AgNPs–EVOH monolith as a SERS substrate, 4-mercaptobenzoic acid (MBA) was selected as a target analyte. We immersed the monolith into 10 mL of ethanol solution containing 10^{-5} M of MBA for 2 h. After post-treatment of the monolith (Fig. S2†), the SERS spectrum of the monolith was measured by using the equipment as showed in Fig. S3.† SERS spectra of MBA collected from 10 randomly selected positions of the monolith are shown in Fig. 4. A peak

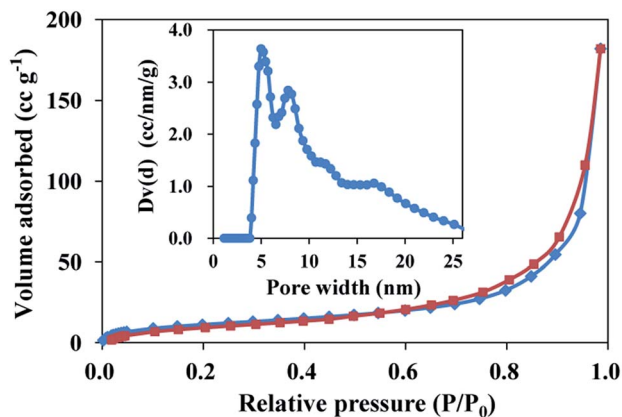


Fig. 2 Nitrogen adsorption/desorption isotherms of AgNPs–EVOH monolith. Adsorption points are marked by blue tetragons and desorption points by dark red tetragons.

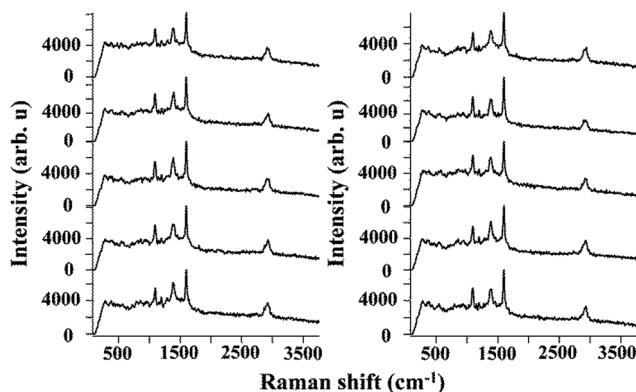


Fig. 4 Series of SERS spectra measured in the randomly selected 10 places on the AgNPs–EVOH monoliths.



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