



## Research Paper

# A silver-grafted sponge as an effective surface-enhanced Raman scattering substrate



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## ABSTRACT

A silver film is *in situ* grafted on a melamine sponge via the silver mirror reaction. The porous structure of the sponge possesses an enlarged total SERS-active surface area without increasing the overall footprint of the SERS substrate. The Ag-grafted sponge exhibits high SERS activity toward Rhodamine 6G with a concentration down to 0.1 pM. Moreover, the sponge-based substrate also offers a good signal uniformity and reproducibility with a relative signal deviation down to 11.7% and 13.2%, respectively. Furthermore, the Ag-grafted sponge exhibits a limit of detection of 4.23 nM toward adenine and 1.88 nM toward thiram in the aqueous solution by a handheld portable Raman spectrometer. The inexpensive and simple Ag-grafted sponge can be used as an effective SERS substrate, which will find the potential application in field-deployable detection of organic pollutants in the aquatic environment.

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## 1. Introduction

Surface-enhanced Raman scattering (SERS) has emerged as one of the most promising techniques for detection of trace chemicals. In particular, it can nondestructively provide the information of fingerprints of target molecules [1–4]. For plasmonic nanostructures, the nano-sized areas (usually in the sub-10 nm gaps) with strongly enhanced electromagnetic (EM) fields are called “hot spots”, which make a significant contribution to the Raman signal enhancement [5,6]. Great efforts have been devoted to colloidal nanoparticles (NPs) [7–10] to generate high-density “hot spots”. In the real-world detection, the morphologies of the metal NPs dramatically change under a high power irradiation or subjected to an aqueous solution, leading to unstable SERS signals [11–13]. To improve the stability of SERS activity, the efficient strategy is modifying the metal NPs with the protective layers [14–16], such as organic layer, or metal layer, so that the SERS sensitivity is greatly dependent on the thickness of outside layers. However, it is difficult to precisely control the uniformity and thickness of the coating layers. To improve the SERS signal reproducibility, intense SERS researches have been pio-

neered, such as the microfluidic systems [17,18] and ordered array patterns [19–21]. The practical applicability is limited by the poor stability due to the oxidation and sulfuration of silver exposure to air [22,23]. To date, great attempts have been developed to wrap Ag nanorods with protective overlayers to enhance the stability by virtue of the atomic layer deposition method [24–27].

A number of flexible SERS substrates have been fabricated using various templates, such as polymers [28,29], elastomers [30,31], papers [32,33], carbon fibers [34,35] and graphene [36]. However, these film-like materials usually work as frameworks to load large quantities of noble-metal nanostructures on a two-dimensional (2D) plane, resulting in relatively low detection sensitivity. Because laser excitation and Raman scattering have a certain penetration depth [37], it is better to design a three-dimensional (3D) SERS substrate to increase the volume of laser-sample interaction without increasing the SERS substrate footprint or the laser beam size. The commercial melamine sponge is an ideal scaffold with high absorption porosity and flexible elasticity [38,39]. Recently, Shin et al. have reported the Au-NPs incorporated with the sponge as a SERS substrate [40].

Inspired by the previous work, a simple, scalable and low-cost approach is devised to develop a Ag film grafted melamine sponge as a 3D flexible SERS substrate via the silver mirror reaction, as illustrated schematically in Fig. 1. The porous Ag film grafted sponge

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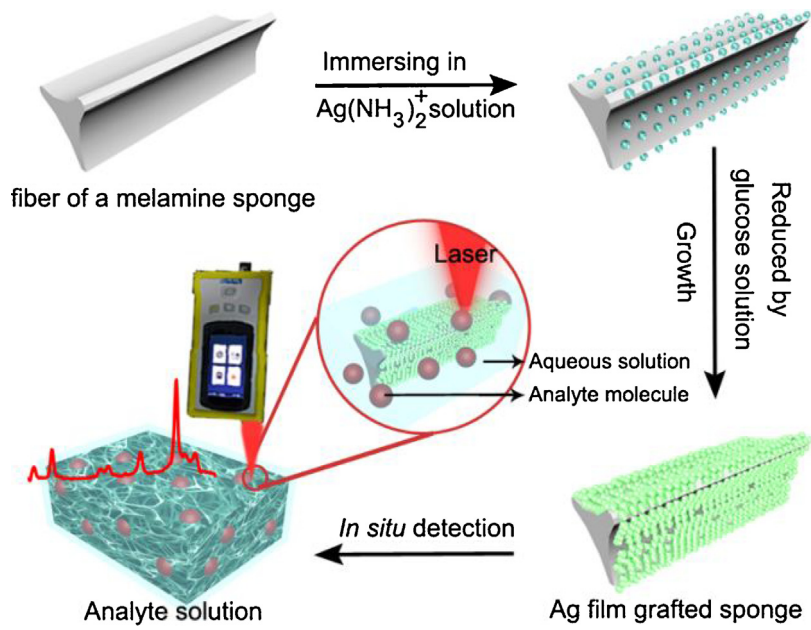


Fig. 1. Schematic illustration of the fabrication process of the Ag-grafted sponge.

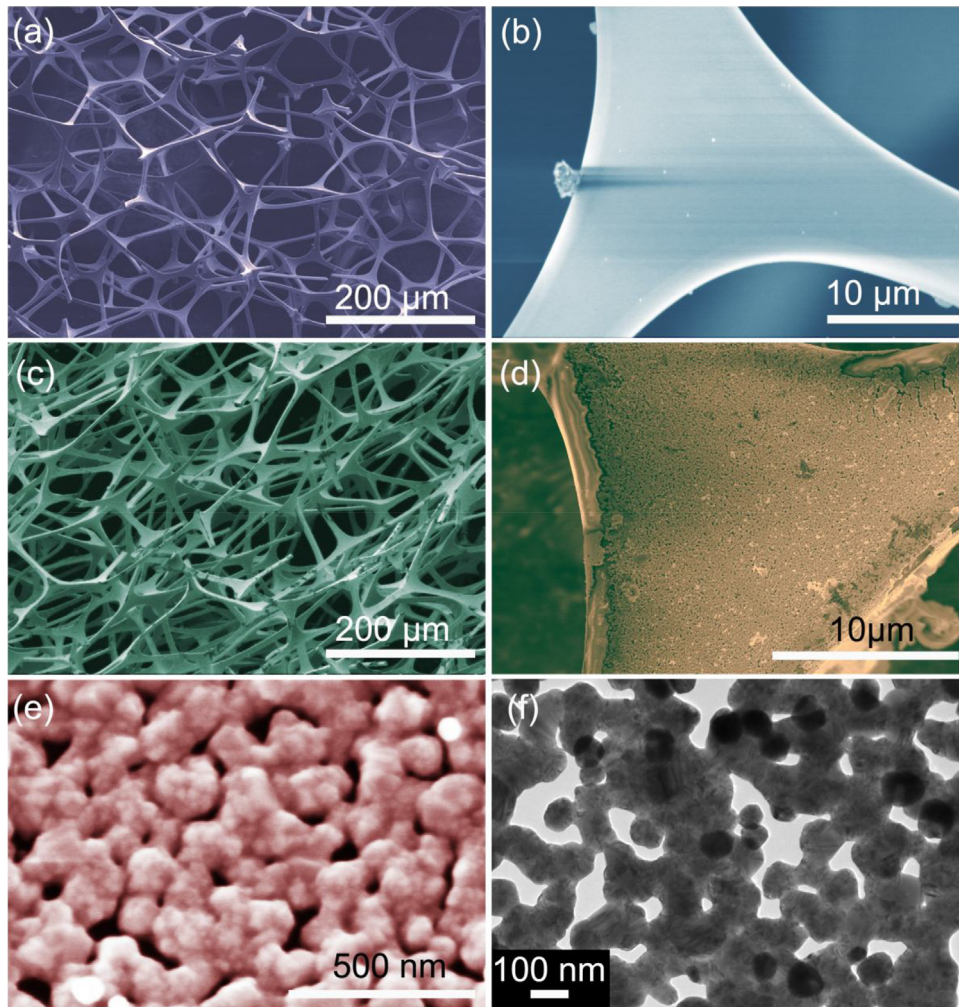


Fig. 2. SEM images of (a) the bare melamine sponge. (b) an enlarged view of (a). (c) the Ag-graft sponge. (d, e) the enlarged views of (c). (f) TEM image of the Ag film exfoliated from the sponge shown in c.

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