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Fabrication of highly-specific SERS substrates by co-precipitation of functional nanomaterials during the self-sedimentation of silver nanowires into a nanoporous film†

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In this report, we propose and demonstrate the fabrication of a highly-specific SERS substrate, which was achieved by the co-precipitation of functional materials, such as nanosorbents and nanocatalysts, into Ag nanoporous films. Based on the nanostructures developed, we performed the ultrasensitive detection of arsenic ions by SERS and monitored the catalyzed reactions using real-time SERS.

Since its discovery in the 1970s,¹ surface enhanced Raman scattering (SERS) has been a research topic of continual interest. Relative to other spectroscopic tools, SERS is novel due to its aptness to provide single-molecule fingerprint spectra,² minimal sample preparation requirements, ease of operation, high tolerance to aqueous samples, and greater adaptability as compared to other methods. As a result, SERS has been widely applied in various fields that range from the *in situ* investigation of catalytic reactions³ to the *in vivo* studies of biological processes at a single-cell level.⁴ Because the SERS phenomenon primarily occurs on the near-field of a SERS substrate, integrating the system of interest with a SERS substrate is of central importance. In simple cases, SERS can be used to observe probe molecules with well-defined morphology,⁵ or hierarchical ensembles of probe molecules with precisely designed configurations, when they are directly anchored to nano objectives (as SERS substrates) made from plasmonic noble metals (Au, Ag, and Cu).⁶ In other occasions, especially in the use of SERS to study chemical or biological processes, conferring the target with SERS activity is considerably more complicated, though this can be partially achieved *via in situ* generated Au/Ag particles,^{4e} or by borrowing SERS activity from an implanted substrate.^{3c,d} One strategy for the use of SERS is to design what we term a “task-specific SERS substrate,” *i.e.*, a SERS substrate designed with a specific functionality to achieve a desired task. However, the uneven and imprecise

implantation of other materials into SERS hotspots, where the majority of SERS is generated,⁷ makes this strategy less effective. The only successful example of this approach is a report where Au or Ag nanoparticles (NPs) were anchored onto graphene oxide (GO) or reduced GO (rGO) to capture an analyte with low affinity for Au or Ag.⁸ Although ultrasensitive detection was achieved for the target molecule, the Raman signal of GO/rGO was slightly enhanced.^{8c}

One solution to this problem is to fabricate three-dimensional (3D) Au or Ag nanoporous films (NPF) as SERS substrates using a bottom-up approach.^{6d} The abundant nanopores within NPFs are highly SERS active due to their ability to effectively couple the electromagnetic field between ligaments.^{6f} Moreover, these nanopores are ready to accommodate new materials and confer them with SERS activity. In addition, the bottom-up approach used in the NPF fabrication process allows the doped material in a hybrid NPF to be evenly distributed. Herein, we report the first example of a template-free fabrication of Ag NPF from the self-organization of Ag nanowires (NWs).^{6d} As a proof-of-concept, nanosorbent (γ -Fe₂O₃ nanosheets (NSs)) or nanocatalyst (Pd overlayer/branches) was co-precipitated into the Ag NPF. In addition to describing a new route for the fabrication of SERS-active Ag NPF, we developed a group of “task-specific SERS substrates.” In these fabricated hybrid NPFs, the Ag surface was selectively blocked while its SERS activity was well-preserved. This method effectively enhanced the Raman signal of the adsorbed arsenic/arsenite ions (As(III)/As(V)) and facilitated the real-time monitoring of catalyzed reactions.

The physical characterization of the developed nanostructures is presented in Fig. 1, and the experimental details for their fabrication provided in ESI†. The interconnected Ag NWs with diameters of 20–30 nm were prepared using a protocol adapted from our previous work (Fig. 1A).⁹ After the self-organization/sedimentation on any substrate, namely, Si wafer or SiO₂ slide, sub-centimeter sized crack-free Ag NPF were fabricated. The Ag NPF had a thickness of about 3 μ m and consisted of uniform ligaments and nanochannels in the range of 30–50 nm (Fig. 1B, with an average diameter of 36.09 $\pm$ 12.48 nm, and Fig. S1, ESI†). Further analysis showed that the Ag is in its metallic form, with Ag 3d electrons located at 368.2 and 374.2 eV (Fig. 1C1). The XRD pattern revealed that the Ag NPF possessed a

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Fig. 1 Morphological and spectroscopic characterization of the fabricated nanostructures: (A) TEM images of Ag NWs; (B1–B3) FESEM images of Ag NPF at different magnifications; (C1–C3) XPS, XRD and UV-vis extinction spectra of Ag NWs and Ag NPF, respectively; TEM and FESEM image of Ag NPF- γ -Fe $_2$ O $_3$ (D and E) and Ag@Pd NPF (F and G).

face-centered cubic structure, which is in good agreement with ICDD card data. Moreover, based on Scherrer line broadening analysis, the size of the ligaments was ~ 32 nm, which is consistent with FESEM inspection (Fig. 1C2). The UV-vis extinction spectra of the Ag NWs showed two pronounced peaks at ~ 340 and ~ 385 nm (Fig. 1C3). The shoulder around 340 nm (marked by the red arrow) was attributed to the plasmon resonance of bulk silver, which results from the network character of the Ag NWs.^{6b} The extinction around 385 nm and above 500 nm were presumably attributed to the transverse plasmon band and the longitudinal plasmon band of Ag NWs, respectively. However, for the further interconnection of NWs, no significant peak was identified in the Ag NPF.

As illustrated in Fig. 1D and Fig. S2 and S3 (ESI[†]), after directly injecting FeCl $_3$ into the freshly synthesized Ag NWs, large areas of γ -Fe $_2$ O $_3$ NSs were formed (see discussion, Fig. S3 and S4 in the ESI[†]).¹⁰ Intriguingly, some nanoparticles with diameters of 20–50 nm were also present on the NSs. These particles were residual Ag NPs that did not connect into Ag NWs, and their adsorption onto γ -Fe $_2$ O $_3$ NSs could serve to provide an additional SERS substrate, thus facilitating the SERS detection of adsorbed As(III)/As(V) ions. After co-precipitation with Ag NWs, a uniform film was formed (Fig. 1E). Surprisingly, in the presence of γ -Fe $_2$ O $_3$ NSs, the film displayed a light green colour, whereas the pure Ag NPF showed the characteristic colour of bulk Ag (Fig. S2, ESI[†]). We attribute this phenomenon to the constrained interconnection of Ag NWs by the incorporated γ -Fe $_2$ O $_3$ NSs. In addition to the metal oxide, a catalytic active transition metal, Pd, was also integrated into the Ag NPF, both in the form of an overlayer and NWs/branches (Fig. 1F and G and Fig. S5 and S6). The formation of an epitaxially grown Pd overlayer is supported by the presence of Moiré patterns that arise from the superposition of

mis-fitted Pd and Ag crystalline lattices.¹¹ In addition to the Pd overlayer, FESEM observations revealed that some Pd NWs/branches anchored on Ag NWs were also precipitated into Ag@Pd NPF.

The high extinction coefficient of Ag NPF in the vis/NIR range indicates that the Ag NPF would display high SERS activity under laser excitation at different wavelengths. Moreover, its 3D nanoporous structure may embody Raman hotspots such as nanopores/nanogaps, nanojunctions, and nanowells.^{6d,f} In addition, good uniformity of the NPF is important for generating reproducible SERS spectra. To demonstrate the SERS performance of Ag NPF, point-by-point Raman mapping was performed on a randomly selected $400 \times 400 \mu\text{m}^2$ area of a Ag NPF loaded with 10^{-8} M thiophenol (TP) (step size of $5 \times 5 \mu\text{m}^2$, 6561 spectra). Fig. 2A shows an SERS intensity at 1077 cm^{-1} , attributed to the phenyl ring mode of TP, under laser excitation at 785 nm. The homogeneous distribution of the intense Raman signal strongly supports the notion that the Ag NPF is uniform over a large area and is capable of generating an SERS signal with good reproducibility. Furthermore, the intensity distribution of the SERS peak at 1077 cm^{-1} excited at 785, 633 and 532 nm, and the corresponding relative standard deviations (RSD) of 13.4, 17.8 and 18.5%, respectively again confirm the homogeneity of Ag NPF (Fig. 2B and Fig. S9, ESI[†]). It is worth noting that there is no apparent wavelength dependence of the Raman signal because there is no change in relative intensity at different excitation wavelengths. This exceptional uniformity and fairly large enhancement of SERS signal make Ag NPF an ideal detection platform for single-molecule vibrational spectroscopy using low-cost SERS sensors.

The potential utilization of Ag NPFs in ultrasensitive SERS analysis was further corroborated *via* single molecule detection (SMD) of crystal violet (CV). As shown in Fig. 2C, discriminable SERS spectra were achieved for CV to a concentration as low as 10^{-11} M, and the calculated enhancement factor reached 5.5×10^8 or above when excited at 532 or 633 nm. Furthermore, 25 out of 1000 spectra

Fig. 2 (A, B) SERS mapping at 1077 cm^{-1} excited at 785 nm and the intensity distribution under different excitation wavelengths. (C) Representative SERS spectra of CV at various concentrations, and (D) SERS spectra of 10^{-6} M AFTs and 10^{-8} M AFT B1, whose characteristic Raman bands have been marked with “*”.

from a Ag NPF loaded with 10^{-13} M CV were identified as the SERS spectra of CV, again confirming the SMD capacity of the Ag NPF (see discussion and Fig. S10 and 11 in the ESI†). In addition to SMD for CV, high sensitivity was also demonstrated for analytes, such as aflatoxins (AFTs),¹² which are toxic contaminants frequently found in crops and other foods. Because the structural resemblance of different AFTs results in spectral similarity, the direct spectroscopic differentiation of AFT G₁, G₂, B₁, and B₂ based on their SERS spectra is challenging (10^{-6} M, described in Fig. 2D). The distinguishable spectrum of B₁ at very low concentrations (10^{-8} M) reveals the advantage of employing SERS in fast screening of AFTs.

Unlike Raman probes or pure chemicals found in the laboratory, samples for real-world applications are complicated to analyze by SERS due to very low concentrations of target analytes and potential contamination with other chemicals. Therefore, selective enrichment of target analytes is of interest. For this purpose, we developed Ag NPFs doped with γ -Fe₂O₃ NSs that showed superior As(III)/As(V) ion capture performance.¹⁰ We evaluated the ability of these fabricated Ag NPF- γ -Fe₂O₃ NSs to detect As(III)/As(V) ions from water samples. As(III)/As(V) ions were captured from water samples (5 mL) containing $10 \mu\text{g L}^{-1}$ As ions, which is the recommended maximum allowable value for drinking water as set by the WHO/USEPA. The captured ions were then analyzed using a portable Raman spectrometer (Enwave Optronics, Inc. USA). In addition to the Raman peaks of γ -Fe₂O₃, *i.e.*, 380, 460, and the broad peak at 1350 cm^{-1} , we observed new peaks from As-O at 796 cm^{-1} and 730 cm^{-1} for As(V) and As(III), respectively (Fig. 3A). The partial oxidation of As(III) was attributed to either γ -Fe₂O₃ induced chemical oxidation or photo-oxidation during SERS analysis. The feasibility of employing Ag NPF- γ -Fe₂O₃ NSs for quantitative SERS analysis of As(V) was further validated by the discriminable peak for $1.0 \mu\text{g L}^{-1}$ of As(V) and the linear relationship between As(V) concentration and the area of the peak at $\sim 800 \text{ cm}^{-1}$ (Fig. 3B and C).

A series of experiments were performed to verify that As(III)/As(V) was adsorbed on γ -Fe₂O₃ and that the Ag surface was blocked by AgCl.¹³ A strong Cl⁻ signal was observed on the Ag NPF- γ -Fe₂O₃ NSs (Fig. S4, ESI†). Because γ -Fe₂O₃ did not adsorb Cl⁻ (data not shown), and considering the high affinity of Ag for Cl⁻, it is reasonable to assign the detected Cl⁻ signal to the AgCl on the Ag surface. The existence of the AgCl layer was further supported by the following experiments. During the formation of Ag NPF, an equal amount of Cl⁻ (0.6 mM) was added, and a strong Cl⁻ signal was detected on the fabricated Ag NPF. However, no AgCl was observed in the corresponding XRD pattern (Fig. S7, ESI†), suggesting that the AgCl was present as a thin layer on the Ag NPF surface. We also compared the SERS performance of the three probe molecules, whose affinity for Ag is in the order of As(V) < SCN⁻ < aminothiophenol (ABT), on Ag NPF (Cl) and Ag NPF. It is interesting to note that the existence of AgCl on Ag NPF has a negligible effect on the SERS activity of Ag NPF; this was verified by the comparable signal intensity of the probe molecule CV (Fig. S14, ESI†). The relationship between the binding strength and SERS intensity indicated the presence of a AgCl layer on the Ag NPF(Cl): (i) only a small fraction of the total As(V) ions can be adsorbed onto Ag NPF(Cl), resulting in a ten-fold lower SERS intensity; (ii) some Cl⁻ ions can be replaced by SCN⁻, resulting in an increased SERS intensity that is still lower than that of Ag NPF;

Fig. 3 (A) SERS spectra of $10 \mu\text{g L}^{-1}$ As(III) and As(V) captured on Ag NPF- γ -Fe₂O₃ NSs; (B, C) background-subtracted SERS spectra of As(V) and the corresponding peak area as a function of concentration; (D) tolerance of SERS detection of $7.5 \mu\text{g L}^{-1}$ or $0.1 \mu\text{M}$ of As(V) to interference from co-existing ions on Ag NPF- γ -Fe₂O₃.

(iii) however, for its strong binding with Ag and replacing the Ag-Cl bond with Ag-S or Ag-N, almost identical sensitivity was achieved for ABT (Fig. S15, ESI†). Therefore, an AgCl layer does exist on Ag NPF, and its existence would constrain the direct adsorption of As(III)/As(V) ions onto Ag. The cooperation between SERS-active Ag NPF and As(III)-adsorbing γ -Fe₂O₃ is therefore the pivotal mechanism responsible for superior As ion detection. Moreover, the SERS detection of As(III)/As(V) is largely unaffected by co-existing ions, with the exception of HPO_4^{2-} (Fig. S16, ESI†), an anion that has similar adsorption behavior as As(V) ion. Together, these data demonstrate the successful fabrication of a SERS substrate for As(III)/As(V) detection (Fig. 3D).

In addition to its frequent application in analytical chemistry, SERS is becoming an important detection method in areas such as operando SERS monitoring of catalyzed reactions.^{3d} To study the application of SERS for operando studies, Pd was deposited on a Ag surface, and its presence was verified by SERS detection of 2,6-dimethylphenylisocyanide (2,6-DMPI), whose potential in distinguishing the surface composition of bimetallic nanoarchitecture is well-acknowledged.^{3d,14} Fig. 4A illustrates the evolution of the SERS spectra with increasing amounts of Pd, where the peak at 2167 cm^{-1} was attributed to the 2,6-DMPI anchored on Ag atoms. This peak exhibited a red-shift to ~ 2110 or $2005/1970 \text{ cm}^{-1}$ after binding to Pd atoms. The former peak was ascribed to atop bonded 2,6-DMPI, and the doublet peak near 2000 cm^{-1} was ascribed to the bridge-bound 2,6-DMPI. We tentatively assigned the peak at 2110 cm^{-1} to the Pd layer and the peak at 2000 cm^{-1} to the Pd NWs/branches on the Ag NWs (see the ESI). The uniformity of Pd on Ag@Pd NPF is demonstrated by SERS mapping, and the ratio between 2167 and 2110 cm^{-1} was employed as an indicator (Fig. 4B and C).

To evaluate the ability of this task-specific SERS substrate to monitor catalyzed reactions, we performed an operando study of Pd-catalyzed *p*-nitrothiophenol (*p*-NTP) reduction. After being loaded with *p*-NTP, the Ag@Pd NPF-deposited SiO₂ slide was adhered to a lab-built reactor and the enhanced Raman spectra

Fig. 4 (A) Evolution of the SERS spectra of 2,6-DMPI with increasing amount of Pd; (B, C) uniformity of Pd on Ag@Pd NPF as shown by SERS mapping; (D, E) 3D SERS mapping recorded on *p*-NTP-loaded Ag@Pd NPF (800 spectra, 0.5 s per spectrum) and calculation of the corresponding rate constant by a first-order reaction model.

were consecutively collected from the same location. The real-time 3D reaction trace is shown in Fig. 4D. Upon addition of 0.2 mM KBH₄, the predominant Raman features of *p*-NTP, ~1340 and ~1570 cm⁻¹, quickly decayed in the first 150 s and disappeared within 450 s, followed by the emergence of a new band at 1590 cm⁻¹. These results demonstrate how Ag@Pd NPFs may be used to monitor chemical processes *in situ*. Moreover, no SERS signal associated with 4,4'-dimercapto-azobenzene (DMAB), a plausible intermediate of this reaction, was observed. Fig. 4E shows the plots of $-\ln(I_{1340(t)}/I_{1340(t=0)})$ as a function of reaction time, where $I_{1340(t)}$ represents the SERS intensity at 1340 cm⁻¹ at different times. The reaction kinetics on Ag@Pd NPF can be divided into two stages, both of which are first-ordered. Furthermore, the difference in deduced kinetic constants signifies the existence of different active centres. The first/fast period is likely catalyzed by the Pd layer on Ag, whereas the slow period can be explained either by the transfer of *p*-NTP from the Ag surface to a nearby Pd atom and its reduction near the Pd atom,^{3c,d} or by the conversion of *p*-NTP on Pd NWs/branches. However, most of the Ag surface was blocked by Pd, as shown in Fig. 4A, suggesting that the slow reaction occurred on the Pd NWs.

In conclusion, we have developed a new method for the fabrication of Ag NPF as a SERS substrate from the self-deposition/organization of Ag NWs. The Ag NPF demonstrated favorable SERS performance, as seen by its large area uniformity, its successful performance in SMD of a dye molecule and high sensitivity detection of AFTs. Compared to other methods for SERS substrate fabrication, the proposed template-free procedure has numerous advantages including low cost and ease of operation. Furthermore, because the Ag NPF fabrication process is compatible with co-sedimentation, we proposed and demonstrated the design of a group of new task-specific SERS substrates generated by co-precipitating nanomaterials, such as nanosorbents and nanocatalysts, into the Ag NWs. The fabricated hybrid nanoarchitectures allowed us to perform ultra-sensitive SERS detection of As(v) ions

with high tolerance for co-existing ions. We also conducted an operando survey of a catalyzed reaction. The reported method can be applied to plasmonic metal NWs, such as ultrathin Au NWs, and can also incorporate other materials into Au NPF (Fig. S17, ESI†). In our laboratory, we are currently investigating the feasibility of incorporating living cells into biocompatible Au NPF for *in vivo* SERS monitoring of biological events at a single-cell level.

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