

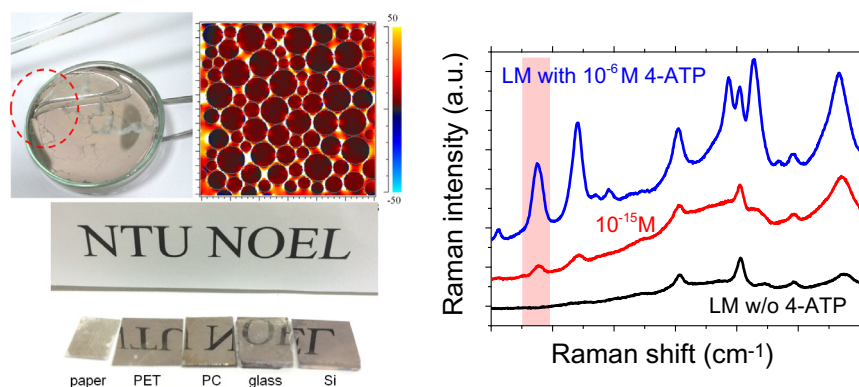
Astronomical liquid mirrors as highly ultrasensitive, broadband-operational surface-enhanced Raman scattering-active substrates



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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we found that an astronomical liquid mirror can be prepared as a highly ultrasensitive, low-cost, highly reproducible, broadband-operational surface-enhanced Raman scattering (SERS)-active substrate. Astronomical liquid mirrors are highly specularly reflective because of their perfectly dense-packed silver nanoparticles; they possess a large number and high density of hot spots that experience a very high intensity electric field, resulting in excellent SERS performance. When using the liquid mirror-based SERS-active substrate to detect 4-aminothiophenol (4-ATP), we obtained measured analytical enhancement factors (AEFs) of up to 2.7×10^{12} and detection limits as low as 10^{-15} M. We also found that the same liquid mirror could exhibit superior SERS capability at several distinct wavelengths (532, 632.8, and 785 nm). The presence of hot spots everywhere in the liquid mirror provided highly repeatable Raman signals from low concentrations of analytes. In addition, the astronomical liquid mirrors could be transferred readily onto cheap, flexible, and biodegradable substrates and still retain their excellent SERS performance, suggesting that they might find widespread applicability in various (bio)chemical detection fields.

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1. Introduction

Because surface-enhanced Raman scattering (SERS) is one of the most important analytical techniques for characterizing molecules in a non-destructive and highly sensitive manner [1], studies aimed at enhancing the intensities of Raman scattering signals continue to receive much attention [2]. Two types of SERS

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enhancement mechanisms have been developed previously: electromagnetic (EM) and chemical (CM) enhancement [3,4]. EM enhancement results from the increased local electric field (E-field) for EM resonances in metallic structures. Regions featuring high E-field intensity, generally known as “hot spots”, are usually located in gaps between adjacent metallic nanostructures [5–7]. The Raman scattering signal can be amplified dramatically with an E^4 dependence; indeed, the enhancement factors (EFs) for EM enhancement have been reported to exceed 10^{10} [7,8]. In contrast, CM enhancement results from the electronic resonance of charge transfer between adsorbed molecules and the surface of the substrate. The reported EFs for CM enhancement have been only in the range from approximately 10^1 to 10^3 [9–12]. Therefore, increasing the Raman scattering signal through EM enhancement is, by far, a more effective way of improving Raman technology.

To increase the applications of Raman technology, a key challenge is the production of low-cost, large-area, highly sensitive, broadband-operational, and reproducible SERS-active substrates that feature a high density of hot spots with huge local E-fields. Larger E-fields in those hot spots will generate larger Raman scattering signals; moreover, a higher density of hot spots will increase the possibility of analytical molecules being adsorbed nearby. For example, a previous study of a silver nanoparticle (Ag NP)-based SERS-active substrate revealed that although only less than 1% of analytes were located at “hot” sites, they contributed almost 70% of the Raman scattering signal; at the same time, 61% of the analytes were located at “cold” sites, yet contributed only 4% to the signal [13]. Thus, enhancement of the overall Raman scattering signal will be limited if none of the analytes are located near hot spots. In addition, a low density of hot spots will also mean that even a slight variation in the location of the analytes will have a significant effect on the overall Raman scattering signal, resulting in SERS signals having poor repeatability [14]. Therefore, a large number and very high density of hot spots is necessary for the fabrication of highly sensitive and reproducible SERS-active substrates. Many approaches have been developed previously to fabricate SERS-active substrates. Optical antennas are popular structures used to generate hot spots with highly local E-fields in the small gaps between pairs of metallic structures or very sharp metallic tips [8,15–17]. When incident light is applied to an optical antenna, the excited surface plasmon (SP) wave at the surface of the metal can concentrate at a position producing a highly intense local E-field. This large local E-field can significantly increase the Raman scattering signal of an analyte located directly at that hot spot. Unfortunately, the preparation of optical nanoantenna structures usually requires complicated processes and expensive instruments, such as electron beam lithography or focused-ion beam (FIB) methods [8,15,17]. In addition, the volume density of hot spots at gaps or tips is usually low over the entire substrate, resulting in very low probability of the analytes being located at these hot spots [14].

Another approach for the fabrication of SERS-active substrates is the use of roughened metallic nanostructures [7,18–22]. This method involves deposition of noble metal films onto substrates featuring desired morphologies, such as textured silicon substrates [7,18,19], anodic aluminum oxide [20], or glass pillar arrays [21,22]. The hot spots that exist in the gaps between adjacent metallic structures can lead, for example, to the EF increasing on the order of 10^7 for rhodamine 6G (R6G) [20]. In addition, the density of hot spots can be very high when using a densely textured structure as the template [20]. Nevertheless, this approach requires some complicated processing, vacuum deposition systems, and special substrate materials.

Although colloidal solutions of metallic NPs can be inexpensive and convenient SERS-active substrates, a key challenge is bringing the NPs sufficiently close to form highly SERS-active hot spots.

Among the several reports of the use of synthesized metal colloidal suspensions for SERS applications [23–26], the self-assembly of metal NPs with an interparticle spacing of less than 10 nm has been notable, leading to enhanced Raman scattering signals with EFs of up to 10^4 for R6G [23] and 10^8 for crystal violet (CV) [24].

In this present study, we used astronomical liquid mirror technology to develop a highly ultrasensitive SERS-active substrate. In the past, liquid mirrors have mainly been developed as reflective optical components within astronomical telescopes, because they are readily deformed to desired parabolic shapes upon application of an external field [27]. Mercury (Hg) was the first material used for the preparation of liquid mirrors because of its high reflectivity and liquid state at room temperature [28]. Unfortunately, toxicity and volatility are serious problems for Hg-based liquid mirrors [29]. To overcome these issues, Yogev and Efrima developed metal liquid-like films (MELLFs) for use in astronomical optics [30,31]. When they added a reducing agent into a chloroform or dichloroethane solution containing silver nitrate and anisic acid, they observed a highly reflective metallic NP film forming at the water–organic solvent interface; these Ag NPs were very densely packed and were spread evenly over the large surface area of the liquid. Nevertheless, a liquid mirror might also feature many tiny gaps in its structure, even between densely packed Ag NPs. As mentioned above, such small gaps between adjacent metallic nanostructures can result in hot spots that lead to increased intensities of Raman scattering signals. Furthermore, the large number and high density of hot spots in a liquid mirror make it highly probable that analytes will be located near these hot spots, thereby dramatically enhancing the overall Raman scattering signal. Hence, liquid mirrors should be very good candidate materials for SERS applications.

2. Experimental section

2.1. Sample preparation

To investigate SERS performance on liquid mirrors, four kinds of SERS-active substrates—three types of self-assembled Ag NP solutions and a Ag thin-film-based mirror—were prepared to compare their surface morphologies, optical properties, and SERS performance. Schematic representations of the three types of Ag NP solutions are displayed in Fig. 1a–c. First, the method developed by Wang et al. was used to prepare the self-assembled NP solution [25]. As displayed in Fig. 1a, the Ag NPs were self-assembled to form multilayer NP clusters, named herein as “NP stacks”. To prepare the NP stacks, cinnamic acid powder was dissolved in a mixture of ethanol and water (3:7, v/v) to form a 10 mM cinnamic acid solution. Next, 10 mM aqueous silver nitrate (AgNO_3 , 0.3 mL) was added to this cinnamic acid solution (9.7 mL) under stirring. After mixing, 1% aqueous sodium tetrahydridoborate (NaBH_4) was added dropwise until the self-assembled Ag NPs formed NP stacks.

Self-assembled NPs were prepared based on the approach reported by Yogev and Efrima [31], but with different reduction procedures applied to form two types of MELLF with distinct morphologies: a “broken MELLF” (Fig. 1b) and an “astronomical liquid mirror” (Fig. 1c). To prepare the broken MELLF, 0.1 M aqueous NaBH_4 was added dropwise to a stirred mixture of 1 mM aqueous AgNO_3 (100 mL) and 6 mM aqueous sodium citrate ($\text{Na}_2\text{C}_6\text{H}_5\text{O}_7$, 20 mL) until the color of the solution changed to yellowish green. Because NaBH_4 is a strong reducing agent, the reduced Ag NPs were small. Therefore, the MELLF prepared by this method was broken. A similar experimental process was also used to prepare the perfectly packed MELLF, the so-called “astronomical liquid mirror” [32]. We used the same method as reported in our previous study [33]: A mixture of 1 mM aqueous AgNO_3 (20 mL) and 1%

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