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Au Nanoparticle Aggregates Assembled on 3D Mirror-like Configuration Using *Canna generalis* Leaves for SERS Applications

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ABSTRACT

Novel biomaterial based SERS substrates fabricated on *Canna generalis* leaf surfaces is reported. The substrates were fabricated by taking advantage of the unique pattern of the surface micro/nanostructures found on the leaf surface and the activity was demonstrated by using R6G as a model analyte. In one of the cases, a three-dimensional mirror-like configuration was created by sputter deposition of a thin film of Au metal followed by assembly of Au nanoparticle aggregates over them to form a nano-junction. This nano-junction based SERS substrate performed better than another substrate fabricated by simple drop casting of Au nanoparticle solution on the leaf surface, which could be attributed to the enhanced plasmonic interactions between the Au nanoparticle aggregates with the Au thin film. Such facile nano-junction based systems having nanoparticles on 3D mirror-like configurations fabricated on naturally occurring materials can be conveniently used for chemical and biomedical analysis.

1. Main Article

Tailored plasmonic metal based nanostructures are being utilized to couple incident light through excitation of their surface plasmons, which enhance their local electromagnetic fields significantly [1]. It is well known that the optical excitation of the surface plasmon band in an ensemble of individual plasmonic metal nanoparticles can result in a significant increase in the average electromagnetic filed intensities at the surface of the particles [1–3]. It is also reported that the enhancement decreases as the excitation wavelength is shifted away from the surface plasmon absorption band [3,4]. When the plasmonic nanoparticles are present in the aggregated form, their plasmon modes can interact with each other. In such cases, the excitation energy is not distributed uniformly over the particles but is localized in “hotspots”, which are much smaller than the excitation wavelength [5]. This property of concentrating the electromagnetic fields can be utilized for surface-enhanced Raman spectroscopy (SERS) applications. In surface enhanced Raman scattering of molecules adsorbed on these surfaces, extraordinarily enhanced Raman signals are usually observed and are ascribed to the adsorption of the molecules at the hotspots located on the clusters of particles [3,6].

Templating has attracted broad interests in recent years for the variety in their types, their innovative structure, singular properties and a wide range of potential applications [7–9]. It is important to synthesize the template or substrate for the utilization in colloidal science applications as the design of the templates imparts different properties such as large specific surface area, enhanced optical performance and many other important functionalities. As a result, engineered templates have been applied in catalysis, optics and electronics, waste removal and controlled release system in the past decades [7–9]. In addition to the template/substrate design, regulation of the nanostructures is also equally important because the optical and electronic properties are highly dependent on the morphology and size of the nanostructures [10–12]. To enhance the SERS activity, it is important to design and engineer the surfaces, which enable the nanoparticles to assemble in a structured manner, leading to the formation of aggregates, which are desirable for the formation of hotspots and thereby lead to the enhancement of localized electromagnetic fields [13]. Over the past few years, many efforts have been made in the design of high-performance SERS-active substrates for detecting particular analytes [3,13]. Conventional substrate materials are rigid and smooth, such as glass slide, silicon wafers or other planer surfaces, which usually are expensive and unsuitable for real complex surface analysis [6,14–16]. Recently, the emerging flexible substrate materials such as paper, cotton, and polymer materials fabricated by different techniques have been explored with an incredible potential for SERS [17–20]. Few reports also exist, where the natural hierarchy of fauna and flora were utilized to assemble and concentrate the plasmonic nanoparticles to further increase the SERS performance [21–23]. While the potential applications of flexible SERS substrate materials are numerous, it is still

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difficult to detect analytes from complex surfaces, improve sampling efficiency and avoid the use of the expensive and exhaustive materials. This motivation has driven us to develop a flexible, eco-friendly, facile and inexpensive SERS substrate for rapid and efficient detection of analytes.

In this work, we have developed a novel biomaterial based SERS substrate fabricated on *Canna generalis* by combining the surface architecture of the leaf surface and the plasmonic nature of Au nanoparticles (Au NP). The surface micro/nanostructures of the leaf surface leads to the formation of nanoparticle aggregates, thus leading to the increase in the number of hotspots, which offer highly efficient detection of the analytes. Furthermore, the design of the substrate was improved by coating the surface of the leaf by a thin layer of Au by sputter deposition and assembling the Au NP over them in a nanoparticles on three-dimensional (3D) mirror-like configuration. Our experimental results have shown that the fabricated SERS substrates can be used in efficient detection of analyte molecules with good enhancement factors (EF). The proposed SERS substrates are promising candidates for practical applications, such as on-site trace detection of analytes in food safety, disease detection, environmental monitoring and homeland security.

In the first step of fabrication, the leaves were fixated with glutaraldehyde and the water content in the leaves was replaced by glycerol to make the samples stable, preserve surface topography, prevent them from dehydration and conserve them for the longer duration of time. In our work, Au NP of size ~100 nm was used for the fabrication of the SERS substrates. For the second step, two different types of methods were employed to fabricate the SERS substrates. In the first method, the Au NP were directly drop casted over the fixated leaf surface and allowed to dry in a desiccator at ambient conditions. In the second method, the fixated leaves were sputter coated with the thin layer of Au (~5 nm) followed by the deposition of the Au NP via drop casting and allowed to dry in a desiccator at ambient conditions. The detailed experimental procedures are discussed in the supporting information and the fabrication process is shown in scheme 1. The SERS substrates fabricated using the first method were named as CG1 and those fabricated using the second method were named as CG2.

Fig. 1 (a) shows the photograph of the C. generalis in its natural habitat. The leaf surface shows hydrophobic nature, which is evident from the contact angle value shown in the inset of the Fig. 1(a). The SEM image of the fixated *C. generalis* leaf is shown in Fig. 1(b). It can be clearly seen that the micrometer level folds are present on the surface, due to the epidermal cells, which form a nice pattern. In addition, the presence of 3D sub-micron sized wax crystals in random hierarchy can be evidenced from the magnified image shown as inset in Fig. 1b. Small gaps, in the range of few nm, leads to the formation of air pockets on the surface, due to the 3D arrangement of these wax crystals. These air pockets are responsible for the hydrophobicity of the leaf surface and perfectly complements the theory postulated by Cassie and Baxter [24].

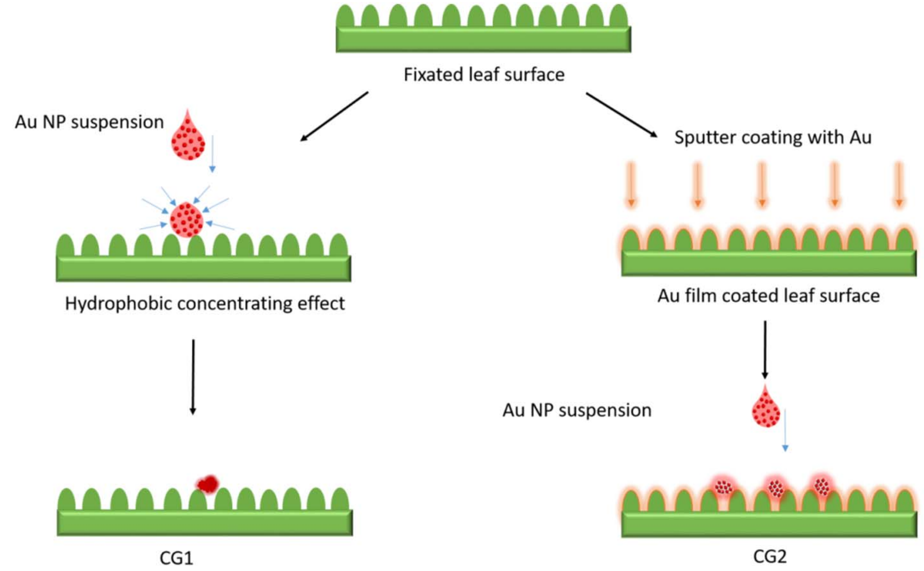
The SEM images of the fabricated SERS substrates are shown in Fig. 2. In case of CG1 shown in Fig. 2(a), dense aggregates of the Au NP ranging from 8 to 20 μm can be seen, which were deposited well between the microfolds of the leaf surface. This dense aggregation of Au NP is due to a phenomenon called hydrophobic concentrating effect, which has been described in detail in one of our previous studies [22]. This dense aggregation leads to the creation of the electromagnetic hotspots due to the interaction of the plasmon bands attributable to the close proximity of the Au NP [22]. Fig. 2(b) shows the SEM image of CG2, where one can see smaller aggregates of the Au NP deposited over the thin Au film coated leaf surface. These aggregates range from ~500 nm to 5 μm in size and are well accommodated by the three dimensional sub-micron structures present on the surface, which were responsible for the aggregation of Au NP in small clusters. It is noteworthy to mention that after the sputter deposition of Au over the leaf surface, there was decrease in hydrophobicity, which can be attributed to the formation of thin Au film on the surface [25].

The SERS performance of both CG1 and CG2 SERS substrates were evaluated using Rhodamine 6 G (R6G) dye as a model analyte. Fig. 3 compares the SERS spectra of R6G dye molecules on CG1 and CG2 SERS substrates under identical conditions. The most prominent features in the spectra correspond to the characteristic modes of R6G [15], observed at 615 cm^{-1} (C—C—C ring in-plane bending), 774 cm^{-1} (C—H out of-plane bending), 1310 cm^{-1} (C—O—C stretching), 1368 cm^{-1} (C—C stretching), 1511 cm^{-1} (C—C stretching), 1573 cm^{-1} (C—C stretching) and 1647 cm^{-1} (C—C stretching). Slight shifting of the characteristic peaks were also observed, which can possibly be attributed to the charge transfer interaction between R6G and Au NP aggregates [15]. The EF for R6G on the two substrates, CG1 and CG2, were calculated mainly considering three peaks at wavenumbers 1368 cm^{-1}, 1511 cm^{-1} and 1573 cm^{-1} which are presented in Fig. 4.

The surface EF was calculated using the equation [26]:

$$\text{EF} = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}}$$

where, I_{SERS} is the intensity of enhanced spectrum, C_{SERS} is the



Scheme 1. Fabrication process of the CG1 and CG2 SERS substrates.