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Zinc oxide/silver nanoarrays as reusable SERS substrates with controllable 'hot-spots' for highly reproducible molecular sensing

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A B S T R A C T

Hypothesis: The reproducible surface enhanced Raman scattering (SERS)-based sensing of an analyte relies on high quality SERS substrates that offer uniformity over large areas. Uniform ZnO nanoarrays are expected to offer an appropriate platform for SERS sensing. Moreover, since ZnO has good photocatalytic properties, controllable decoration of silver nanoparticles on ZnO nanoarrays may offer an additional opportunity to clean up SERS substrates after each sensing event.
Experiments: This study employs a facile soft chemical synthesis strategy to fabricate Raman-active and recyclable ZnO/Ag nanorod arrays as reproducible SERS substrates. Arrays of ZnO nanorods were synthesized using hydrothermal method, which was followed by controllable decoration of ZnO with silver nanoparticles (AgNPs) using an electroless plating technique.
Findings: The uniform density of SERS-active 'hot-spots' on ZnO nanoarrays could be controlled on a large 1×1 cm^2 substrate. These ZnO/Ag nanoarrays showed high reproducibility (0.132 RSD) towards acquiring SERS spectra of rhodamine B (RB) at 30 random locations on a single substrate. The photocatalytic nature of ZnO/Ag semiconductor/metal hybrid endowed these substrates with reusability characteristics. By controlling metal loading on a semiconductor surface, photocatalytic activity and high SERS performance can be integrated within a single package to obtain high quality, reproducible, stable and recyclable SERS substrates.

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1. Introduction

Surface enhanced Raman scattering (SERS) has attracted considerable attentions due to its high sensitivity, non-destructive nature and ability to provide information about the structure of the trace materials [1,2]. Particularly, this technique has shown remarkable sensitivity in detecting low concentrations of analytes, sometimes even up to single molecule detection by enhancing the Raman intensity of the analyte molecules with the aid of noble metals [3,4]. Despite the on-going developments, SERS has not yet gained full acceptance as a quantitative analytical spectroscopy technique [1,5,6]. This is predominantly because the development of highly stable SERS substrates that can generate reproducible SERS spectra across large surface areas remains elusive. Two interrelated considerations that may bring SERS technique to the mainstream sensing techniques include (i) materials engineering to develop appropriate SERS-active materials that can provide high SERS sensitivity [3,7,8], and (ii) substrate engineering to achieve controllable distribution of SERS-active material on substrates for high reproducibility [8–13]. The former aspect is important as the size, morphology, composition and crystallinity of SERS-active nanomaterial makes a major contribution to the Raman enhancement [14]. The latter is equally important from the reproducibility perspective as it is now well-recognized that the Raman enhancement can significantly vary from spot-to-spot within a single SERS substrate, dependent on the change in the topology or the surface roughness [15]. While lithography techniques have been used successfully to control the substrate topology, the cost- and time-expensiveness of these techniques make them less preferable for mass production of SERS substrates [11]. When the aforementioned two aspects of materials and substrate engineering are combined together, the interparticle spacing of the SERS-active material on the substrate surface becomes equally critical, as this spacing is known to create

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'hot-spots' for high SERS enhancement [16–18]. Therefore, for obtaining an appropriate SERS enhancement as well as high sensing reproducibility, the density of these 'hot-spot' and their uniform distribution on the designed substrate should be increased.

Besides, recent efforts are directed towards adding additional functionalities to the SERS-active materials, such as fabrication of a magnetite core/SERS-active metal shell nanostructure for targeting and separation of the cancer cells [19] and SERS-coded gold nanorods for near infrared imaging [20]. Another important functionality that may be added to the SERS-active substrates is the reusability characteristic, which is important as the SERS substrates are currently used typically only for a single sensing event. This self-cleaning ability may, in principle, be achieved by combining the photocatalytic ability of a semiconductor such as titania with the Raman enhancement ability of metal nanoparticles [21–24]. If the loading of SERS-active metal nanoparticles onto semiconductor surface is appropriately controlled, the photocatalytic performance of the semiconductor also improves, as these metal clusters act as electron sinks to reduce the charge (electron–hole) recombination post-photon excitation [25,26]. Further, the semiconducting material may also contribute to the improvement of SERS response through charge transfer (CT) between the semiconductor surfaces and the analyte [27]. This suggests that it is possible to achieve both optimum photocatalytic and SERS performances from a single hybrid semiconductor/metal material by finely controlling its structure and composition.

Among different semiconductors, ZnO offers a good choice of material to fabricate desirable SERS-active substrate because (i) it is a wide band-gap material with proven outstanding photocatalyst performance [28,29] to offer self-cleaning attributes and (ii) it can be regularly fabricated in the form of uniform nanorod arrays [30] that may assist in obtaining reproducible SERS response. Among different metals, silver nanoparticles (AgNPs) appears to be a good choice as it is considered the most powerful material for SERS enhancement [14,31] and it also has the proven ability to enhance the photocatalytic activity of semiconductors [7,25]. However, since ZnO is unstable under highly acidic or alkaline environments, most of the previous efforts on growing metal nanostructures on ZnO nanoarrays have relied on physical deposition methods [32]. These physical deposition methods offer low controllability in terms of uneven distribution of metal nanoparticles, resulting in drastic reduction in the reproducibility of the SERS spectra throughout the substrate surface. Therefore, in an effort to achieve a self-cleaning reproducible SERS substrate, we report a facile, highly controllable and inexpensive soft-chemical method to fabricate AgNPs-coated ZnO nanoarrays (ZnO/Ag). This study demonstrates that the controllability of AgNPs loading on ZnO nanoarrays allows optimum tunability between the high and reproducible Raman enhancements while providing sufficient photocatalytic activity to build self-cleaning attributes in these novel SERS substrates.

2. Materials and methods

2.1. Materials

All the chemicals were purchased from Sigma Aldrich and used as received. Si (0 0 1) substrates (1 cm × 1 cm) were employed for the growth of ZnO nanoarrays, which were cleaned using sequential washing and ultrasonication in acetone, ethanol and isopropanol before drying under nitrogen. Further, to eliminate any remaining organic traces from the Si surface, the substrates were exposed to UV–Ozone (UVO Cleaner Plus) for 10 min. Deionized MilliQ water (18.2 MΩ m) was used throughout the synthesis process.

2.2. Fabrication of Si/ZnO nanorod arrays

Si wafers were coated with a uniform ZnO thin film via sol–gel process [33]. Briefly, 15 mL ethanolic solution of 0.1 M zinc acetate dehydrate was mixed with monoethanolamine (MEA) in equal weight ratio, followed by aging the mixture at 55 °C for 24 h and spin coating 300 μL of this solution on to Si wafers at 3500 rpm for 15 s. The substrates were dried at 95 °C for 10 min and the spin coating procedure was repeated five times before annealing the substrates at 450 °C for 1 h to achieve uniform and dense ZnO thin film on Si substrates.

For the hydrothermal growth of ZnO nanorod arrays, 50 mL solution containing equimolar (0.05 M) aqueous zinc nitrate hexahydrate and hexamine was transferred to sealed glass autoclaves. The substrates were floated on the top of the solution in the autoclaves such that the ZnO thin film side of the substrate faced the solution. The hydrothermal reaction was allowed to proceed for 6 h at 95 °C, followed by collecting the Si/ZnO nanorod array substrates and rigorous washing with deionized water before drying with N_2 gas under ambient conditions.

2.3. Decoration of Si/ZnO nanorod arrays with AgNPs (ZnO/Ag nanoarrays)

ZnO nanorod arrays (1 cm × 1 cm) were decorated with AgNPs using an electroless deposition method, wherein initially ZnO was sensitized for 30 min with a 2 mL aqueous solution containing 0.3 mM $SnCl_2$ and 0.1 μL trifluoroacetic acid. After washing with water, substrates were immersed in 2 mL of 3 mM aqueous $Pd(NO_3)_2$ for 10 min to form Pd nuclei that acted as seeds for silver plating in the next step. The density of AgNPs on the surface of Sn- and Pd-sensitized ZnO nanorod arrays was controlled by exposing these substrates initially to different concentrations (1, 10, 100 and 1000 mM) of 1 mL diaminesilver(I) complex ($[Ag(NH_3)_2]^+$) [34], followed by addition of 1 mL glucose (1 M) to reduce this complex at room temperature. The substrates were collected after 1, 3 and 6 min of reaction, washed with water and dried under N_2 gas prior to further use.

2.4. Substrate characterization

SERS substrates were characterized using different microscopic and spectroscopic techniques. Morphological studies were performed using field emission scanning electron microscope (SEM – FEI Nova NanoSEM), X-ray diffraction (XRD) patterns were collected using Bruker AXS X-ray diffractometer using Cu Kα radiation, X-ray photoelectron spectroscopy (XPS) surface analyses were carried out by a Thermo Scientific K-Alpha instrument using un-monochromatized Mg Kα radiation (photon energy 1253.6 eV) under vacuum better than 10^{-9} Torr, and XPS core levels were aligned to the adventitious C 1s binding energy (BE) of 285 eV.

2.5. Evaluation of SERS activity

Rhodamine B (RB) was selected as a model probe molecule to evaluate the SERS activity of the prepared substrates. RB was bound to the substrates by immersing substrates independently in 1 mL of 100 μM RB for 1 h in the dark, followed by rinsing the substrates with deionized water and air drying. Raman spectroscopy measurements were performed using Perkin Elmer Raman Station 200F (785 nm laser) with a spot size of 100 μm, 5 s exposure time and 10 acquisitions averaged with background correction feature disabled. The backgrounds of Raman spectra were corrected using an in-house developed algorithm [35]. Since ZnO is a wide band-gap semiconductor with an optical absorption edge of ∼370 nm, 785 nm laser source was used for SERS studies so that