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Self-assembled Au nanoparticle arrays on thiol-functionalized resin beads for sensitive detection of paraquat by surface-enhanced Raman scattering

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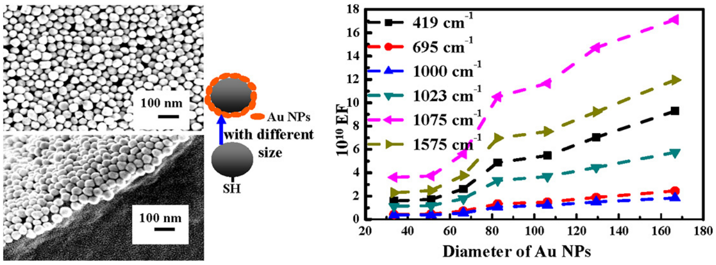
HIGHLIGHTS

- Creation of thousands of plasmonic Au NPs–resin core–shell spheres per gram.
- Scalable fabrication under mild conditions without using any expensive equipment.
- Each as-synthesized Au NPs–resin sphere could be an easy-to-use SERS substrate.
- Higher reproducible enhancement effect enabled by densely well-ordered Au NPs.
- Qualitative detection of pesticide paraquat with a low detection limit of 10^{-12} M.

GRAPHICAL ABSTRACT



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ABSTRACT

Efficient, scalable, and cost-effective self-assembly of Au nanoparticles (NPs) into close-packed arrays on the surfaces of thiol-functionalized resin spheres under mild conditions was demonstrated. The resulting Au NPs–resin spheres possessed a structure in which the densely packed Au NPs monolayer and the resin bead are the shell and the core, respectively. Each Au NPs–resin sphere could be used as a surface-enhanced Raman scattering (SERS) substrate with high SERS-enhancing capacity and reproducibility. The SERS enhancement factor (EF) was estimated at 10^9–10^{11} by using thiophenol as the probe. The spatial and sphere-to-sphere variations in SERS EF were <18%. The SERS-enhancing capacity could be tuned by varying the Au NPs size. The detection limit of paraquat in water by SERS using the as-synthesized Au NPs–resin as active substrate was $\sim 10^{-12}$ M. The fabrication method could be a promising alternative to the preparation of well-ordered NPs arrays for SERS-active substrates.

1. Introduction

Surface-enhanced Raman scattering (SERS) is a powerful tool for the analysis of vibration information of analytes, including detection down to near-single-molecule levels [1,2]. The enhancement of Raman signals results from excitation by localized surface plasmons within metallic nanostructures of SERS substrates due to strong electromagnetic and chemical interactions [3,4]. Hence, rationally designed substrates play a crucial role in the application of SERS [5]. SERS substrates can be prepared through either the bottom-up or the top-down strategy. More elaborate top-down strategies have become accessible because of latest developments

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in nanolithography, including the tailoring of nanostructures for maximum enhancement and reproducibility even in large areas [6]. However, the common disadvantage of some of these top-down methodologies is their high cost [7–10].

A cost-effective alternative in the preparation of SERS substrates is self-assembly of metallic nanoparticles (MNPs, bottom-up approach), particularly, two-dimensional (2D) arrays of MNPs supported by flat solid templates [7,11–27] or by polymer beads [25,28-37]. These materials offer the benefit of multiple hotspots generated in a uniform fashion over a larger substrate area, which in turn strongly enhance signals across the substrate. Examples of the most widely used MNPs are wet-processed Au or Ag nanoparticles (NPs) and their assemblies. Surface plasmon resonance (SPR) properties of MNPs may be tailored to provide the greatest SERS enhancement specific to the systems of interest by tuning MNPs composition and structural parameters (e.g., shape and size) [5,6,10,13,16,20,24,25,38,39]. Accordingly, various methods have been established to assemble MNPs, such as solvent evaporation [10,13,17,19,40], in situ formation at interfaces [20,41], the Langmuir–Blodgett technique [42], layer-by-layer assembly [43], and spin-casting [44]. However, some of these approaches have some restrictions or shortcomings that limit their extensive application, such as long processing time, unique equipment, or low throughput. Furthermore, the very high SERS enhancement enabled by noble MNPs is commonly compromised by the poor detection reproducibility caused by the stochastic aggregation of MNPs [45].

To exploit MNPs self-assemblies in technological applications of SERS and to ensure efficient scale-up, a high level of direction and control is required [46]. With the aid of electrostatic attraction [16,23,25,26] or functional chemicals [7,11,12,15,18,21,27–31], Au or Ag NPs could be assembled into well-ordered 2D arrays on the surface of solid templates to form substrates for high-performance SERS. Unfortunately, irregular and low metal coverage on the templates has been typically observed. Very recently, an elegant example of well-ordered 2D arrays prepared by self-assembly of Au NPs into close-packed arrays at liquid/liquid or liquid/air interfaces was reported [9]. Hydrophilic, hydrophobic, or amphiphilic molecules (or a mixture thereof) could be captured and detected individually or simultaneously by such a novel SERS substrate. As the interfacial area of the Au array (~25 mm^2) may be reduced, the array is ideal for small-volume samples. Another example is Au (or Ag) NPs-coated polystyrene (PS) latex beads prepared through a combined swelling–heteroaggregation method [30,31]. In this method, the Raman signals detected are of PS and poly(vinyl)pyrrolidone (PVP), indicating that the Au or Ag NPs are coated with PVP, and are probably inaccessible to the external target analytes. However, it is important that the surfaces of self-assemblies of noble-metal NPs are accessible. Pal [32] reported the synthesis of resin beads with an ultrathin silver nanoshell on commercially available anionic resin beads. The resulting particles could be exploited as SERS substrate by using crystal violet as a Raman probe. However, the quantitative results of SERS enhancement and reproducibility of such substrates have not been reported. On the other hand, polymer beads with dimensions of hundreds of nanometers to tens of micrometers have been used [25,28-37]. From the standpoint of applications, preparation of close-packed arrays of Au or Ag NPs supported by commercially available anion-exchange resin beads should be a cost-effective, scalable, and efficient alternative in the fabrication of MNPs-based SERS substrates.

Herein, close-packed Au NPs arrays were self assembled onto thiol-functionalized, commercially available anion exchange resin beads (~0.8 mm in diameter) to produce robust and cost-efficient SERS substrates (Au NPs–resin, Fig. 1). The SERS enhancement factor (EF) of Au NPs–resin was measured by using thiophenol as the Raman probe. To evaluate the reproducibility of SERS enhancement by Au NPs–resin spheres, the relative standard deviation (RSD) of EFs from both spatial and sphere-to-sphere measurements was calculated. Finally, a method for SERS detection of trace levels of pesticide paraquat (PQ) in aqueous solution using the as-prepared Au NPs–resin as substrate was performed.

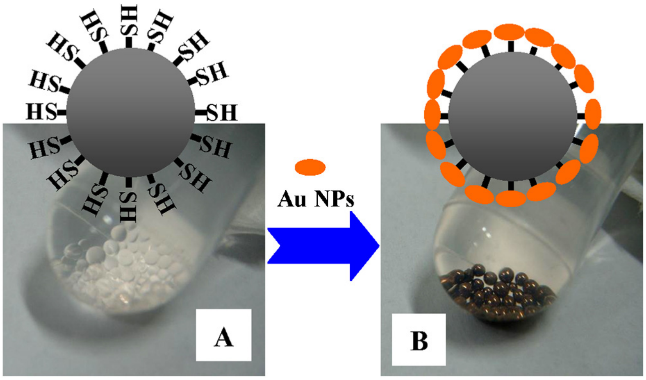

Fig. 1. Schematic illustrating the fabrication process for the Au NPs arrays on thiol-functionalized ion exchange resin beads: (A) HS–resin and (B) Au NPs–resin spheres.

2. Materials and methods

2.1. Synthesis of Au NPs

Monodisperse Au NPs with diameters of 30–170 nm were synthesized through the seed growth method [49]. After centrifugation, the residual Au NPs were washed twice with deionized water, and then were redispersed in methanol to a concentration of 10^9–10^{11} NPs per milliliter [49].

2.2. Fabrication of Au NPs–resin spheres

Commercially available anion-exchange resin beads were completely converted from the Cl-form into the HO-form by using 2 M NaOH aqueous solution. HO-form resin beads were immersed in a thioglycolic acid (TGA)–methanol solution (2 M) for at least 12 h to yield thiol-functionalized resin beads (HS–resin) via acid–base reaction of TGA with OH ions. To fabricate Au NPs–resin core–shell spheres, HS–resin beads (0.02 g) were mixed with the aforementioned Au NPs–methanol dispersion (12 mL) with gentle shaking for 3 h at 30 °C. The mixture was gently sonicated (30–60 s) to remove free Au NPs.

2.3. Characterization techniques

UV–visible spectra of Au NPs were acquired with a Shimadzu UV-2400 spectrophotometer. Au NPs were visualized by transmission electron microscopy (TEM) by using a JEM-2100 operated at an accelerating voltage of 200 kV. Their X-ray diffraction (XRD) pattern was recorded on a D8 Advance X-ray diffractometer that uses graphite-monochromated Cu Kα radiation ($\lambda = 0.154$ nm). Field emission scanning electron microscopy (FE-SEM) on a Hitachi S-4800 was performed to investigate the morphology of Au NPs arrays on the surface of the Au NPs–resin spheres. Raman measurements were performed at room temperature on a Renishaw micro-Raman system microscope with 785 nm laser as excitation source. An area of ~2 μm diameter was probed under a 50× objective lens. The incident power was 25 μW and the acquisition time was 10 s. To evaluate the substrate Raman-enhancing capability of the Au NPs–resin spheres, a traditional Raman probe thiophenol was used. The Au NPs–resin spheres were immersed in