



Synthesis of large flower-like substrates for surface-enhanced Raman scattering

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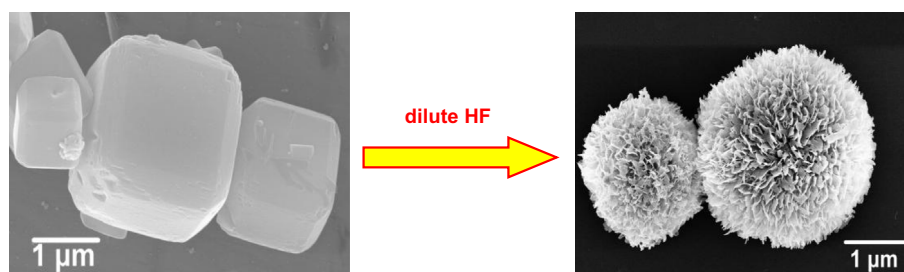
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HIGHLIGHTS

- A new, well-designed type of large flower-like SERS substrate is synthesized.
- The new substrates exhibit high and reproducible SERS enhancement.
- The new substrates are expected to be applied in SERS-based analytical devices.

GRAPHICAL ABSTRACT

A new, well-designed type of large flower-like SERS substrate is synthesized by treating 3 Å molecular sieves with dilute hydrofluoric acid to prepare a support and then plating silver nanoparticles on this support.



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ABSTRACT

A novel type of large flower-like SERS substrate was synthesized *via* a hard template process. The synthesis was performed by etching commercial 3 Å molecular sieves with dilute hydrofluoric acid to prepare a flower-like support followed by the deposition of silver nanoparticles onto the support by chemical reduction. The as-prepared substrates exhibit high and reproducible SERS with an enhancement factor of $\sim 1.4 \times 10^6$, estimated using 4-mercaptobenzoic acid (4-MBA) as a model adsorbate. The method is low cost and avoids the use of nonvolatile surfactants in the preparation process, so may have potential application in the development of SERS-based analytical devices.

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1. Introduction

Surface-enhanced Raman scattering (SERS) is widely used in chemistry, biology, physics and material science since it can enhance the inherently low Raman scattering cross sections of molecules, sometimes even at the single-molecule level [1–3]. SERS enhancement is known to be especially significant when

analyte molecules are adsorbed onto the surface of noble metallic nanoparticles. Relative SERS enhancement factors are sensitive to the size, shape, surface morphology and aggregation state of the metal substrates because the oscillations of free electrons are controlled by the substrate geometry [4–6]. Therefore, rational design of metal substrates has become an important issue for using SERS in routine applications [7–10]. However, in most cases, metallic nanoparticles are prone to aggregation due to Van der Waals forces and high surface energy. Additionally, the aggregation of metallic nanoparticles is random and difficult to control, which results in

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reduced stability of SERS substrates and temporal signal variance in SERS measurements.

Two main methods had been developed to prevent metallic nanoparticles from aggregating. One is to employ polymers, complex ligands or surfactants to modify the surface of metallic nanoparticles [11–17]. However, the polymers or surfactants, which cover the nanoparticle surface, hinder analyte-surface interaction, which may lead to false positive results. In addition, polymers and surfactants have been found to affect the growth rate of different crystal faces, resulting in the formation of anisotropic nanocrystals rather than spherical ones [18–21]. Anisotropic signal enhancement leads to spatial spectral heterogeneity across a given sample surface. The other effective method for stabilizing metal nanoparticles is *via* deposition on certain supports. This immobilization results in the prevention of nanoparticle aggregation, which avoids the requirement to utilize nonvolatile surfactants and polymers. This is also commonly used in nanoparticulate systems for heterogeneous catalysis [22–27].

Recently, the technique of supporting metal nanoparticles on silica spheres was successfully used in the preparation of SERS substrates. For example, Kim et al. fabricated Ag nanoparticles on nanoscale silica beads and demonstrated that the Ag-deposited silica beads were highly efficient SERS substrates, exhibiting an enhancement factor estimated to be larger than 10^6 when using benzenethiol as a model adsorbate [28]. Large scale noble metal substrates with sub-micrometer or micrometer size were also developed and yielded stable SERS signals for detected molecules [29–33]. However, the SERS enhancement factor from these micron-sized particles is attenuated due to higher-order multipolar plasmon modes appearing, as well as the particle size being close to or larger than the excitation wavelength. A strong electromagnetic enhancement could be provided by the introduction of controllable nanoscale roughness onto the particle surface, which can effectively couple to an optical electric field [31].

In this paper we report the design of a new route for preparing flower-like SERS substrates. The process was performed by etching commercial 3 Å molecular sieves with dilute hydrofluoric acid to prepare a flower-like support, followed by the deposition of silver nanoparticles onto this support. These novel substrates exhibit strong and reproducible SERS effects. The enhancement factor is larger than that when silica spheres are used as supports. Most importantly, the substrates are low-cost and can be synthesized on a large scale, while no surfactants or polymers are required during preparation.

2. Experimental section

4-MBA, silver nitrate (>99.8%), ammonia solution (28.0–30.0 wt%), potassium hydroxide (>82%), ethanol (99.9%), and glucose were used in reagent grade and without further purification. The 3 Å molecular sieve was supplied by the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, and was heated for 4 h at 600 °C in a muffle oven and then cooled in a desiccator. Highly pure water with a resistivity higher than 18.0 MΩ cm was used in all the preparations.

2.1. Synthesis of flower-like supports

The lattice structure of the 3 Å molecular sieves consists of SiO₄ and AlO₄ tetrahedra. The reaction of these aluminosilicates with HF to form the flower-like structures is proposed in Eq. (1):



According to Eq. (1), it is reasonable to speculate that the framework of aluminum trifluoride can be formed via treating the 3 Å molecular sieves with dilute hydrofluoric acid. This is because the aluminum trifluoride product is insoluble in aqueous HF while silicon tetrafluoride is.

To yield monodisperse flower-like aluminum trifluoride supports with high surface areas, 3 Å molecular sieves were treated with dilute HF. Specifically, 30 mg of 3 Å molecular sieves were poured into 50 ml of 7 wt% aqueous HF solution under continuous magnetic stirring. After standing for 24 h, the products were separated from the reaction medium by centrifugation at 3000 rpm. After thorough washing with water and ethanol to remove the excess reactants, the products were dried under vacuum at room temperature for 4 h.

2.2. Synthesis of modified flower-like substrates

Silver nanoparticles were anchored onto the aluminum trifluoride supports at a loading of approximately 30 wt% Ag using a modification of the method described by Saito and co-workers [34]. Potassium hydroxide aqueous solution (2.6 wt%, 0.2 ml) was mixed with silver nitrate aqueous solution (2 wt%, 3 ml) to form a fine brown precipitate of Ag₂O. An aqueous ammonia solution (8 wt%) was added dropwise until the precipitate completely dissolved to form [Ag(NH₃)₂]⁺. Silver nitrate aqueous solution was added to the mixture until the solution turned pale brown/yellow. One drop of ammonia solution (2 wt%) was added and the solution became transparent. Subsequently, 90 mg of the flower-like supports were added to the above [Ag(NH₃)₂]⁺ solution with continuous magnetic stirring for 5 min to ensure homogeneous mixing. Formaldehyde aqueous solution (1 ml, 2 wt%) and pure ethanol (0.5 ml) were then added to this mixture. The mixture was kept at 40 °C in a water bath for 1 h. The solid particles were separated from the reaction medium by centrifugation at 3000 rpm. After thoroughly washing with water and ethanol, the powdered product was dried under vacuum at room temperature for 4 h. In order to adsorb 4-MBA on flower-like substrates to perform SERS measurements, the samples were immersed in an ethanolic solution of 4-MBA (18 ml, 1 mM) for 1 h. After thorough washing with water and ethanol to remove the excess reactants, the products were dried under vacuum at room temperature for 4 h.

2.3. Characterization

A variety of methods were used to systematically analyze the composition, structure, and morphology of the as-synthesized flower-like substrates. Field emission scanning electron microscopy (FESEM) of the samples was recorded using a SUPRA35 FESEM operating at 15 kV. Transmission electron microscopy (TEM) was performed using a JEM-1011 microscope operating at 100 kV. The size distribution of the 3 Å molecular sieves was measured with a LS-100Q laser diffraction particle size analyzer. X-ray powder diffraction (XRD) measurements were performed on a D8ADVANCE powder diffractometer over a 2θ range of 5–90° at an angular resolution of 0.02°. X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo VG ESCALAB250 spectrometer with a monochromatic X-ray source of Al Kα (1486.6 eV). Raman spectra were obtained with a Jobin Yvon LabRam HR 800 micro-Raman spectrometer equipped with a microscope (Panasonic Super DYNAMIC). Laser radiation of 632.8 nm was used for excitation. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer.

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