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ARTICLE

A Simple Wet-Chemical Route for the Preparation of Silver Dendrites on Commercial Silicon Wafer and Their Application in SERS Detection

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Abstract: Design and preparation of various rational silver micro-nanostructures has been recognized as a promising solution for the surface-enhanced Raman scattering (SERS) signal amplification. Here, a simple wet-chemical method was reported for the synthesis of high-density Ag dendrites structures on silicon wafer by rapidly mixing silver nitrate and hydrofluoric acid aqueous solutions. The reductive Si-H surfaces are oxidized while silver ions are reduced, yielding a final Ag dendrites structure that offers an excellent SERS enhancement. The EDS measurements confirm the metallic nature of the formed Ag dendrites. Researches also show that the pure and low-cost Ag dendrites are about several micrometers in size and can be rapidly and reproducibly produced in high yield. There are no organic contaminants on the surface of the resulting dendrites structure. Additionally, the influence of experimental parameters on the morphology of dendrites was also investigated, such as hydrofluoric acid concentration, silver nitrate concentration, and the reaction time. Importantly, the fabricated Ag dendrites substrates can be used for accurate and reliable determination of Sudan I, Sudan II, and Sudan III.

Key words: silver dendrites; wet-chemical method; fabrication; SERS

In the past several years, dendritic micro-nanostructures of noble metal have drawn worldwide attention owing to their unique superstructure and attractive physicochemical properties[1]. Silver (Ag), as one of the most common noble metals, has been widely used in many fields including nano-antibiotic material, catalysis, electronic devices, and sensing. In particularly, it has often been considered as the effective material for surface-enhanced Raman scattering (SERS)[2]. Recently, a large number of various silver micro-nanostructures have been reported as ultra-sensitive SERS substrates for the signal amplification. Among them, Ag dendrites structures have attracted researchers' interests because their trunks and branches have unique electromagnetic enhancements[3-5]. As a result, extensive efforts have been devoted to search for novel methods for the preparation of Ag dendrites, for example, vapor deposition[6], electrochemical synthesis[7], hydrothermal/solvothermal methods[8,9], sol-gel approach, and template method[10].

Unfortunately, all these above-mentioned approaches suffer from more or less unacceptable shortcomings such as requiring specialized equipment, time-consuming, high cost, non-environmentally-friendly technology, and easily contaminated with organics, which push the scientist to explore new alternative solutions overcoming such limitations.

Wang et al[2] have fabricated the snow-flake-like Ag dendrites by directly mixing silver nitrate and p-phenylenediamine aqueous solutions. This method was based on an oxidation-reduction process where 4-amino is oxidized while silver ions are reduced. However, it suffers from that the as-prepared Ag dendrites were easily contaminated by the organic reducing agent. Carraro et al[11] have also prepared Ag dendrites with a large surface area-to-volume ratio on Al foil

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via a galvanic displacement. Although it was regarded as a cost-effective approach for preparing SERS-active substrate, the reaction yield is too low (only about 40%).

Here, we developed a simple wet-chemical route for the synthesis of high-density Ag dendrites structures on silicon wafer by rapidly adding silver nitrate and hydrofluoric acid aqueous solutions at room temperature. The resulting Ag dendrites were about several micrometers in size and can be rapidly and reproducibly produced with higher yield. No organic contaminants were found on the surface of the dendrites structure. The influence of experimental parameters including hydrofluoric acid concentration, silver nitrate concentration, and the reaction time on the dendrite formation was also examined. It was also found that the morphology is critical for the SERS enhancement performance. Importantly, the fabricated Ag dendrites substrate was successfully employed for detecting Sudan I, Sudan II, and Sudan III, indicating that they could have a good future for implementation.

1 Experiment

1.1 Preparation of Ag dendrites

The experimental procedures involved the following steps: First, pre-cut silicon substrates (5 cm×5 cm) were sequentially cleaned ultrasonically for 10 min in acetone, ethanol, and deionized water, separately and then dried by nitrogen-blowing. Then, certain silver nitrate and hydrofluoric acid aqueous solutions were rapidly mixed. Next, the treated silicon substrates were placed in the mixed solution carefully. After the reaction finished, the obtained Ag dendrites/silicon substrates were cleaned three times by deionized water and dried immediately by nitrogen-blowing. Finally, the dried Ag dendrites substrates were transferred into a vacuum chamber for further tests.

1.2 SERS detection

A nanofinder flex laser Raman spectrometer (UNISOKU-TII) was used to carry out the SERS measurements. The as-prepared Ag dendrites structures were used as SERS-active substrates. Rhodamine 6G (R6G) was chosen as a model analyte to investigate the performance of the Ag dendrites substrates. Crystal violet (CV) was chosen for the relative standard deviation (RSD) analysis. First, the SERS measurements were performed by dipping the Ag dendrites substrates into 10 mL of R6G aqueous solution (different concentrations from 10^{-4} mol/L to 10^{-12} mol/L) for 4 h. Then, the substrates were washed by deionized water and dried by nitrogen-blowing. The dried Ag dendrites substrates were transferred to Raman test platform for measurements. A 633 nm argon ion laser was used for excitation with a spectral resolution of 1 cm^{-1} and spot size of 1 μm. The laser focused on the surface of substrates was about 1.7 mW. The recorded spectra were raw data without any processing. The Ag dendrites substrates were employed again to detect Sudan I, Sudan II, and Sudan III under the same experimental conditions.

2 Results and Discussion

In order to trace the growth evolution of Ag dendrites during the different reaction time, a series of samples with varying durations were prepared (from 1 min to 120 min), while keeping other parameters exactly the same. Here, we first examined the time-dependent morphology evolution of the resulting Ag dendrites by collecting SEM images with different reaction time of about 1, 2, 10, 30, 60, and 120 min after the mixing of silver nitrate and hydrofluoric acid aqueous solutions (Fig.1). As shown in Fig.1a, a large number of silver worms appear on the surface of the Si substrate during the initial growth stage (the first min). One min later, the worms begin to grow thick and grow up (Fig.1b). However, when the reaction time increases to 10 min, the silver worms gradually change into dendrites (Fig.1c). After 30 min of growth (Fig.1d), the substrate surface is composed of regions with high density of dendrites.

Further increase of the reaction time to 1 h or 2 h (Fig. 1e and Fig.1f), the dendrites are obtained with a thicker trunk and longer branches. It is clear that the length, diameter, and density of the dendrites are accompanied by increasing reaction time. It should be noted that the resulting Ag dendrites remains unchanged after a repeated washing process, which indicates the satisfactory binding force exists in the interface of dendrites and substrate. We also find that each sample (except Fig.1a and Fig.1b) gives quite similar structures to the final Ag dendrites. Besides, the reactions are carried out at room temperature, indicating that the formation of Ag dendrites is a rapid and mild process[12].

The energy-dispersive spectrometry (EDS) analysis of the typical as-grown Ag dendrites for 60 min is displayed in Fig.2. Fig.2a shows the general morphology of Ag dendrites in which a constant angle can be seen clearly between the trunk and branches[13]. Two peaks at 3.0 and 3.2 keV (Fig.2b), reveal the Ag (0) nature of the dendrites[14]. It can be indicated from this spectrometry that the dendrites is composed of silver. The Si element distribution (1.74 keV, ~1.77%) detected from Ag dendrites may be contributed to the silicon substrate and other Ag-Si impurities.

The spontaneous formation of Ag dendrites can be attributed to the direct redox between $AgNO_3$ and the reductive Si-H. Indeed, recent research shows the significance of the formation of Si-H[15]. Generally, it was carried out by chemical treatment of silicon wafer with hydrofluoric acid (1 mmol/L) at room temperature. It is also worth mentioning that 95% silver nitrate is transformed into Ag dendrites, indicating our approach is high yield in nature.

It is well established that an increase of the reactants concentration leads to increased reaction rate and thus a non-equilibrium system being easily built, which is beneficial

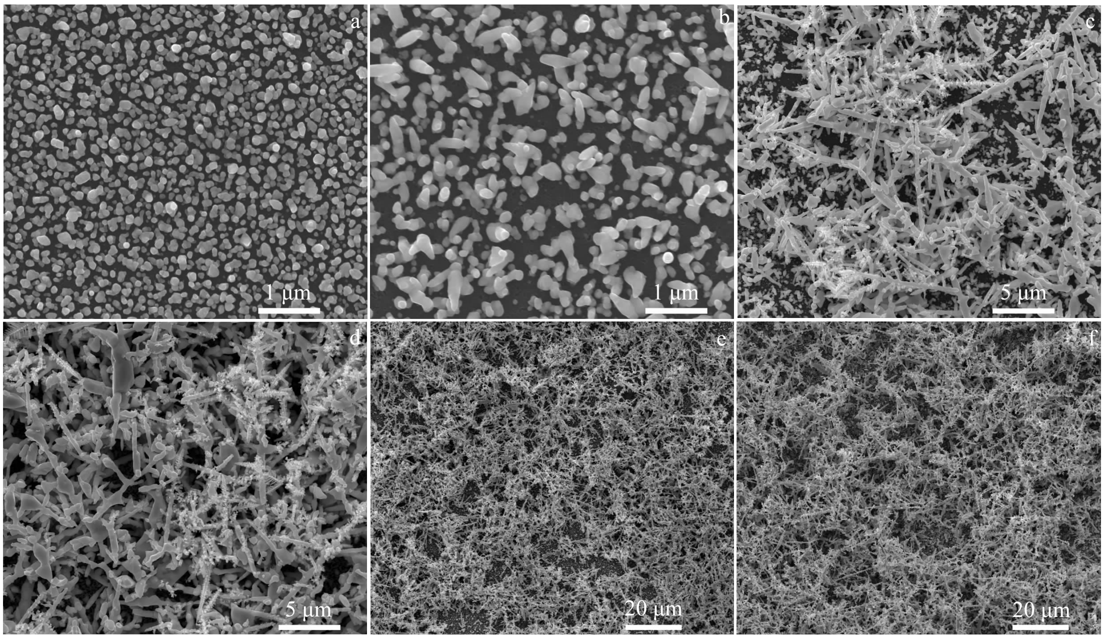

Fig.1 SEM images of Ag dendrites formed with different reaction time of 1 min (a), 2 min (b), 10 min (c), 30 min (d), 60 min (e), and 120 min (f) after the mixing of $AgNO_3$ and HF aqueous solution

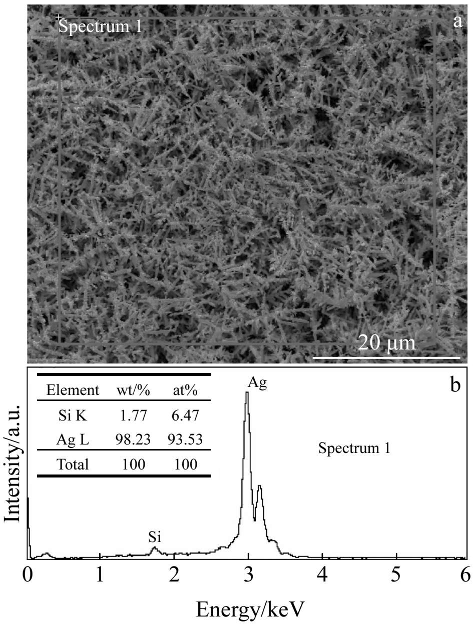

Fig.2 SEM image of the as-prepared Ag dendrites (a) and EDS spectrum of the selected area in Fig.2a (b)

for the formation of Ag dendrites[16]. We speculate that the formation of Ag dendrites is accomplished by the mixing of silver nitrate and hydrogen fluoride aqueous solution. The Ag ion is rapidly reduced by Si-H to form Ag atoms when these two solutions are mixed together. The Si-H surface originates from the silicon substrate which was treated under hydrogen fluoride for several minutes. Here, we performed one control experiment where HF aqueous solution was used as the precursor for the preparation of Si-H weak reducing agent.

The concentration of HF varies from 1.0 mol/L to 6.6 mol/L, and the different Ag dendrites structures are obtained (Fig.3a~3e). All the above observations show that the formation of Ag dendrites is not attributed to the high concentration of hydrogen fluoride (such as 5.2 mol/L and 6.6 mol/L). At much higher concentrations, only a small number of irregular Ag dendrites structures are obtained. However, those fragmentary dendrites structures only exhibit general SERS performance (Fig.3f). When the concentration of hydrofluoric acid is diluted to 2.4 mol/L or 1.0 mol/L, the enhancement property of Ag dendrites SERS substrates are improved dramatically[17].

Furthermore, the density and morphology of Ag dendrites structure can also be effectively controlled via adjusting the contents of silver nitrate. It is very urgent to increase the number of the branches to enhance the localized surface plasmon resonance (LSPR) and the SERS performance. As shown in Fig.4, the SEM images reveal that the increase of branches is accompanied by the increase of Ag ion, which provides a new opportunity to adjust the Ag dendrites structures and their SERS enhancement[18]. Obviously, with more silver scaffolds comes a greater ability for SERS detection (Fig.5).

To test the reproducibility (substrate uniformity) of the as-prepared Ag dendrites, SERS spectra of CV with a constant concentration from ten random-selected sites on the Ag

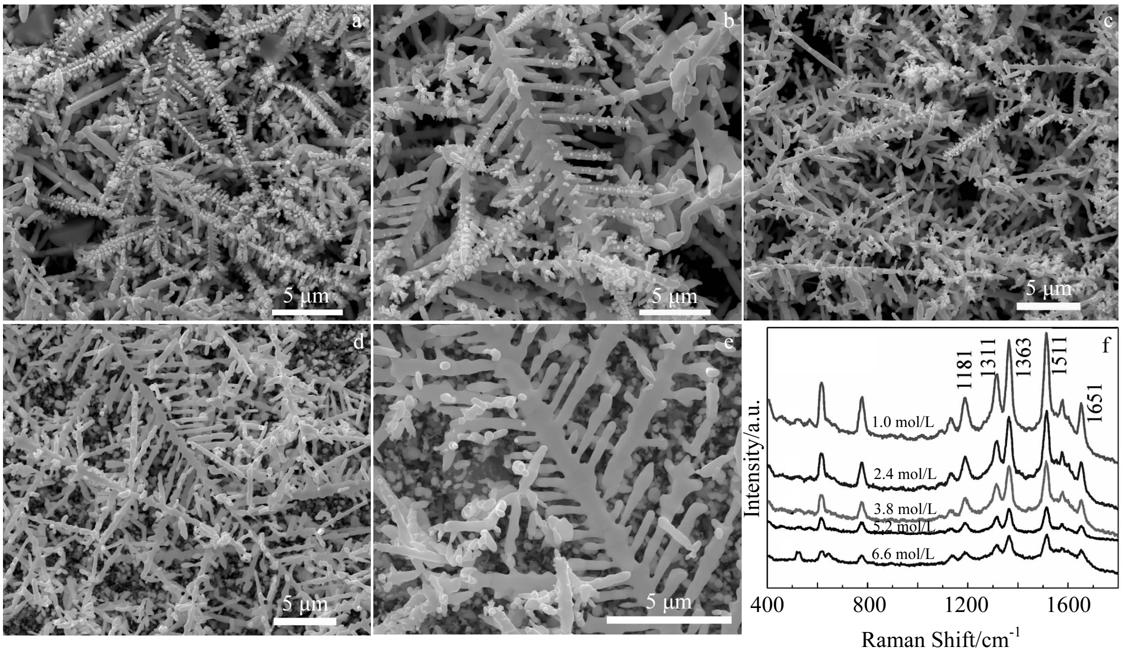

Fig.3 SEM images of Ag dendrites formed under different hydrogen fluoride concentrations: (a) 1.0 mol/L, (b) 2.4 mol/L, (c) 3.8 mol/L, (d) 5.2 mol/L, and (e) 6.6 mol/L; Fig.3f represents the corresponding SERS spectra of R6G analyte based on the different Ag dendrites prepared under corresponding hydrogen fluoride concentrations

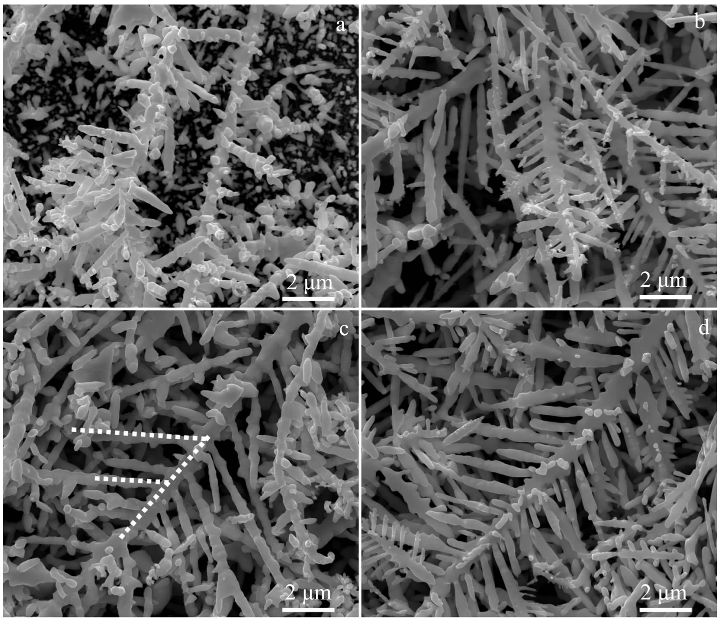

Fig.4 SEM images of Ag dendrites formed under different silver nitrate concentrations: (a) 0.01 mol/L, (b) 0.02 mol/L, (c) 0.05 mol/L, and (d) 0.1 mol/L

dendrites were collected under the same experimental conditions[19]. As shown in Fig.6, these SERS spectra exhibit good similarity. For the peak at 1378 cm^{-1}, the relative standard deviation (RSD) of the SERS intensity is about 12% (a noticeable improvement corresponding to the previous 21.3%), which indicates that the Ag dendrites is rather potential for the sensitive and reproducible SERS sensing[20,21].

In recent years, emerging harmful substances and unapproved additives residues in food or drinking water have attracted people's great attention[22-26]. As shown in Fig.7, the as-

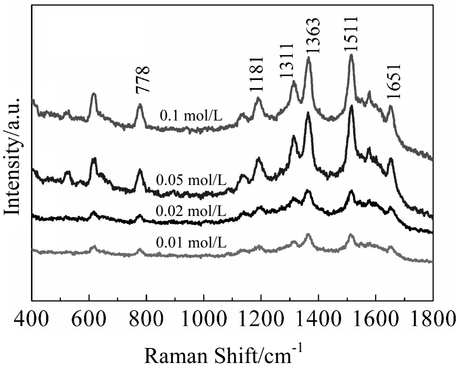

Fig.5 SERS spectra of R6G analyte based on the different Ag dendrites prepared under different silver nitrate concentrations

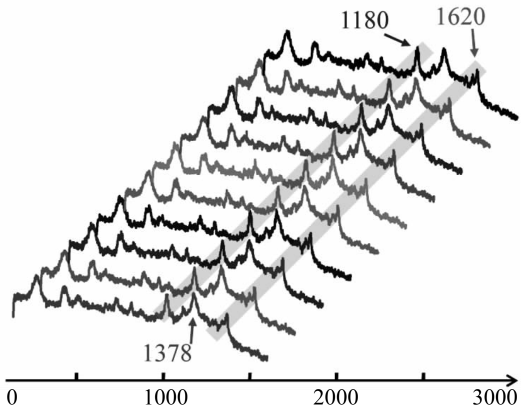

Fig.6 SERS spectra of CV analyte collected from 10 random sites on the as-prepared Ag dendrites (the laser power is 1.7 mW; the exposure time is 10 s)

prepared SERS-active Ag dendrites substrates are employed for the sensitive and rapid detection of Sudan I, Sudan II, and Sudan III. In Fig.7a, curve (I) represents Raman spectra of the Sudan I (1 mmol/L) collected from the reference substrates. Curve (II) shows the SERS spectrum of Sudan I (0.1 μmol/L) collected from the SERS-active Ag dendrites. Although the background fluorescence interference is observed, the main characteristic peaks of Sudan-I are depicted clearly in the SERS spectra. For example, the characteristic Raman bands at 721, 974, 1172, 1219, 1395, 1503, and 1609 cm^{-1} are clearly found, which are assigned to Sudan I unique Raman scattering[27-30]. In addition, the Sudan II and Sudan III are also detected successfully by our Ag dendrites SERS substrates under the same conditions (Fig.7b and Fig.7c). Also, several differences are found among themselves, such as the main peak is assigned to 1172, 1144, and 1133 cm^{-1}. These results indicate that the as-prepared Ag dendrites could be employed for detecting and identifying food additives and has great potential in food inspection, environment monitoring, and other application areas.

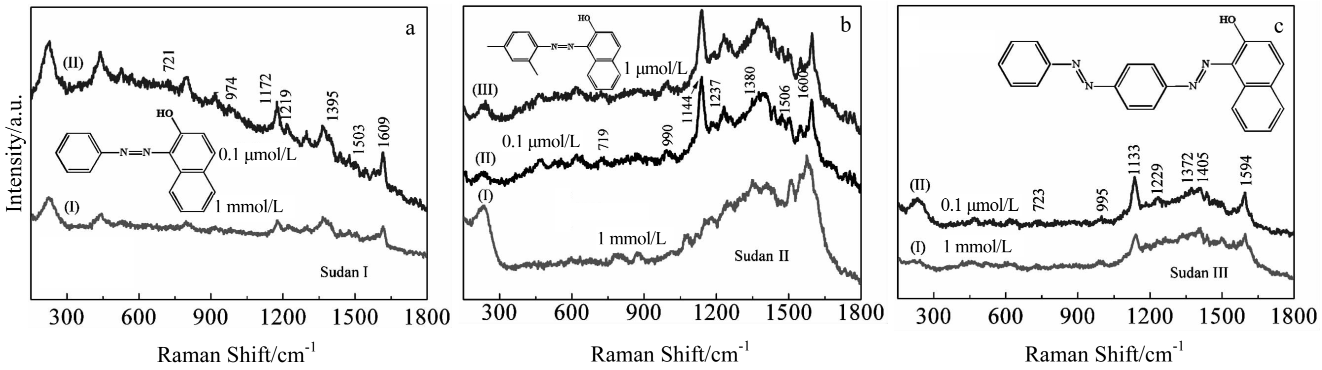

Fig.7 SERS detection of Sudan I (a), Sudan II (b), and Sudan III (c) (curve I is based on Si substrate, curves II and III are based on Ag dendrites substrates)

3 Conclusions

1) A simple wet-chemical route can be developed for the synthesis of high-density Ag dendrites structures on silicon wafer by rapidly adding silver nitrate and hydrofluoric acid aqueous solutions at room temperature. The dendrites morphology is critical for the SERS enhancement.

2) EDS measurements demonstrate the metallic nature of the formed Ag dendrites. The as-prepared Ag dendrites SERS substrates exhibit a good reproducibility for SERS detection (the RSD is 12%).

3) Three typical food additives (Sudan I, Sudan II, and Sudan III) can be detected based on the as-prepared Ag dendrites SERS-active substrates, which indicates a promising application in sensing and analysis areas.

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硅基银枝晶的湿化学法制备及其在 SERS 检测中的应用

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摘　要：设计并构建结构多样的银枝晶一直被认为是一种实现表面增强拉曼散射（SERS）信号放大的合理途径。本文报道了一种简单的湿化学方法，通过快速混合硝酸银和氢氟酸水溶液，进而实现了硅片表面高密度银枝晶的快速制备。由于 Si-H 表面具有一定的弱还原性，随后导致了银离子的还原，并最终形成了具有良好 SERS 增强特性的银枝晶结构。该方法生产速率快，重现性好，产率高，其尺寸通常为微米级，且枝晶表面无任何有机污染物。EDS 分析进一步证实了所制备的枝晶结构为单质银属性。此外，详尽的研究表明所制备的银枝晶结构其形貌与具体的反应参数如氢氟酸浓度、硝酸银浓度以及反应时间等息息相关。重要的是，利用成功制备的该枝晶结构实现了苏丹 I、苏丹 II 和苏丹 III 的快速分析检测。

关键词：银枝晶；湿化学法；制备；SERS

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