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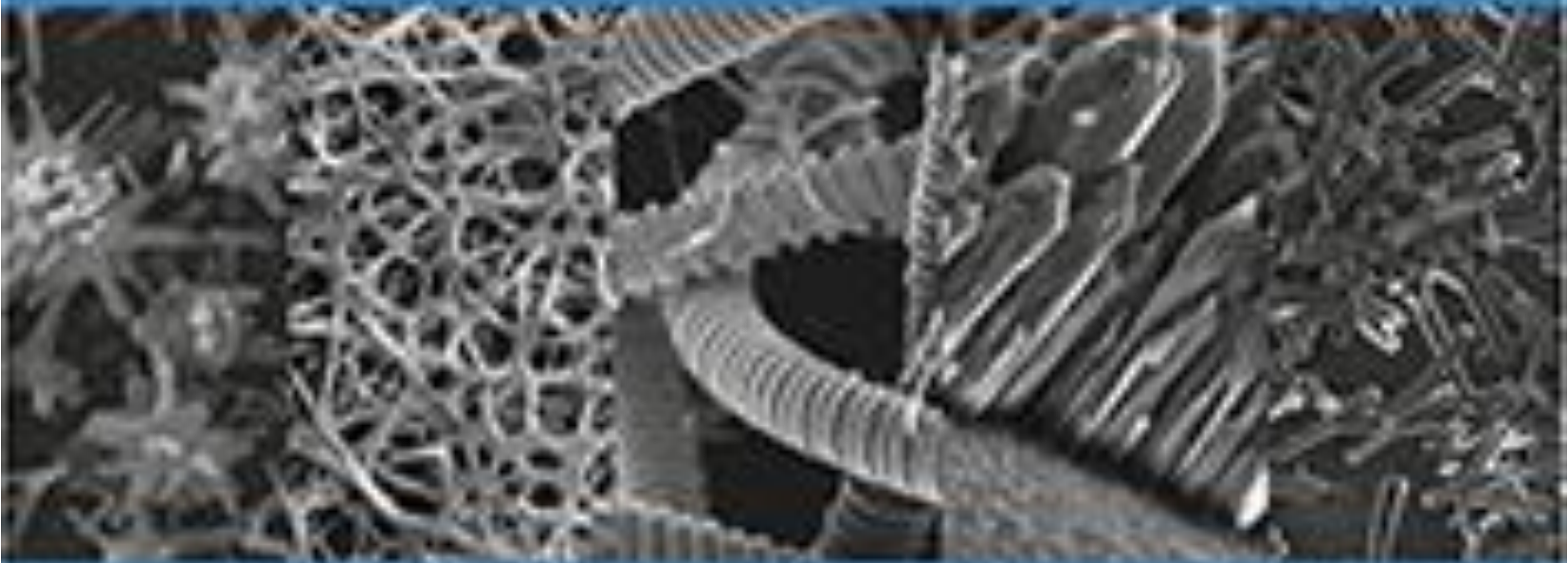

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Preparation of silver fractal nanostructures and their application in surface enhanced Raman scattering

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A B S T R A C T

Three kinds of silver fractal nanostructures were prepared by replacement reaction method using copper, tin, aluminum foils and $AgNO_3$ solution. The dentritic, flower bud and shoot bud silver nanostructures had self-similar structural features. Meanwhile, these silver fractal nanostructures had the same structure characters as proper plants in actual biological systems. Furthermore, these silver fractal nanostructures exhibit high surface enhanced Raman scattering (SERS) activity.

1. Introduction

Surface enhanced Raman scattering (SERS) effect has been applied successfully in various fields, for example, molecular sensing, biomolecule detection, and environmental monitoring [1–3]. Compared to gold and copper nanostructures, silver nanostructures have the advantages of fine conductivity, quantum size effect and high surface enhancement effect [4–6]. Various nanostructured materials are being developed and investigated in SERS sensing applications with a plethora of nanostructures being investigated, such as nanorods, nanowires, nanostars and so on [7–9].

The fractal theory studies irregular geometric shape and is a powerful tool to study the irregular figures in nature and project [10,11]. The fractal growth may appear during the preparation process of metal nanostructures and its theory can be used to reveal the growth mechanism of self-similar shape nanostructures [12,13]. The structural features of fractal indicate that it has great potential in SERS application.

In this study, we used a replacement reaction method [14] to prepare silver fractal nanostructures for application as SERS substrates. The behavior of the SERS activity was consistent with a strong influence of the morphology of the fractal structures. The resulting silver nanostructures can be engineered to possess tailored, hierarchical morphologies and compositions that present opportunities for synthesizing new types of SERS substrates.

2. Experimental

Chemicals, equipment, and experiment procedures can be found in Supplementary materials.

3. Results and discussion

Fig. 1a gives a typical SEM image of silver dentritic nanostructure. The side branches are symmetrically arranged on both sides of the trunk of the whole dentrite. It reveals that the self-similar hierarchical structure expected for a fractal dentrite. Fig. 1b clearly shows that the dentrite is composed of lots of side branches, which have similar structures as the whole structure. Furthermore Fig. 1c indicates that the morphology of the secondary side branches, which shows that the secondary side branches still have similar structure like the whole structure. The biological entity most similar to this dentritic nanostructure may be fern [15]. As shown in Fig. S1 it can be seen that the side branch has a structure similar to the whole branch.

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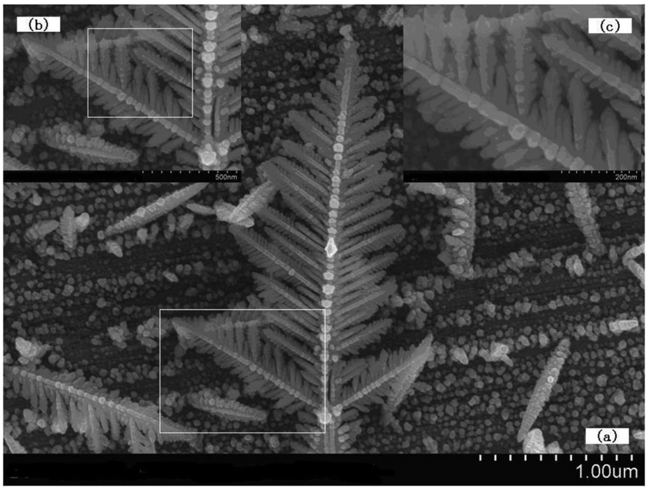

Fig. 1. SEM images of silver dentritic nanostructures on copper foil: (a) The whole structure (b) The structure of side branch (c) The structure of the secondary side branch.

Fig. 2 shows the results of X-Ray Diffraction (XRD) measurements of silver fractal nanostructures. The lattice constants determined from these XRD measurements are a = b = c = 0.4081 nm, very close to the standard value of 0.4077 nm for a silver crystal as obtained from the XRD database. The EDX of the fractal nanostructures shows that the element component is silver (Fig. S2).

Fig. 3 shows the morphology of silver nanostructures on the tin foil. As shown in Fig. 3b, there are flower bud nanostructures at the bottom of the branch. But on the top of the branch, silver nanoparticles are compact and close to spherical flower bud in shape (Fig. 3c). It is mainly composed of flower bud nanostructures, while the individual spherical flower buds are composed of smaller spherical flower buds. Meanwhile, the nanostructures have the same structural characteristics as cauliflower [13] in actual biological systems. The whole and its partial structures of flower buds of cauliflower are similar to each other (Fig. S3).

As shown in Fig. 4, we can see the microscopic morphology of silver nanostructures on aluminum foil. It seems like shoot buds on the substrate and reveals a self-similar structure. Each shoot bud contains smaller shoot bud structures while the smaller shoot bud has a fine structure similar to that of the whole shoot bud. In actual biological systems santolina chamaecyparissus [16] exhibits the same morphology configuration as this nanostructure (Fig. S4). Santolina chamaecyparissus contains many shoot buds which consist of lots of smaller shoot buds.

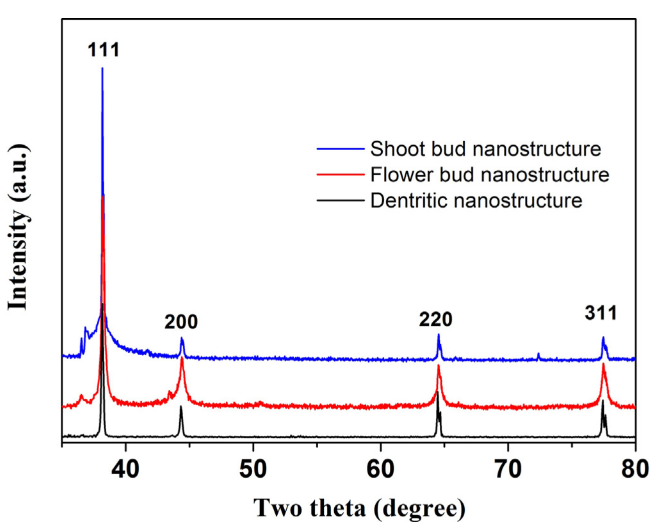

Fig. 2. XRD of silver fractal nanostructures.

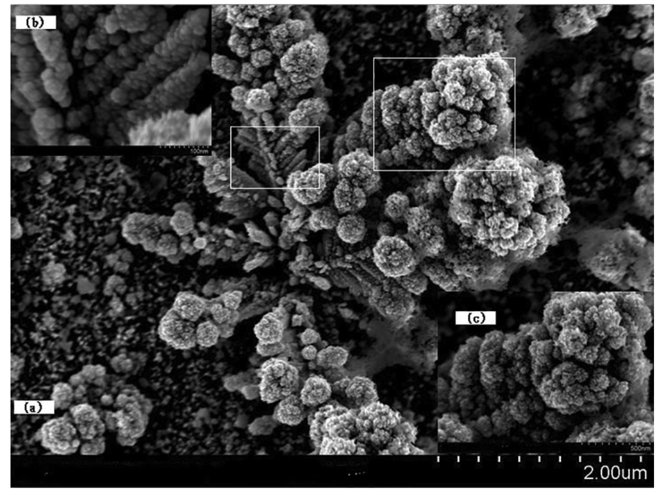

Fig. 3. SEM images of silver nanostructures on tin foil: (a) The whole structure; (b) The bottom structure of the branch; (c) The top structure of the branch.

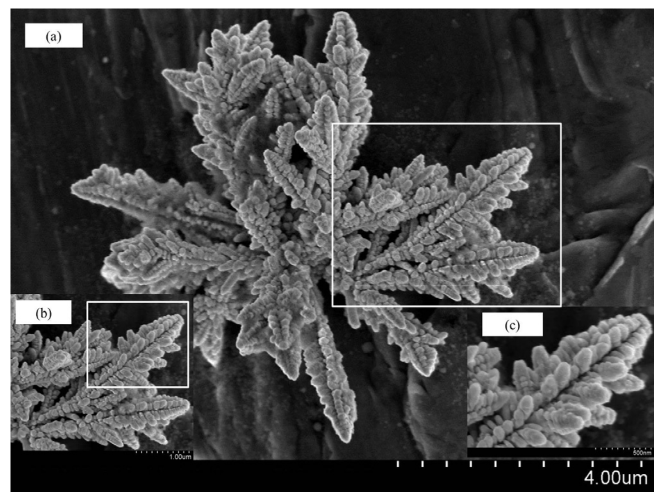

Fig. 4. SEM image of silver nanostructures on aluminum foil: (a) The whole structure (b) The structure of side branch (c) The structure of the secondary side branch.

We also studied the products in the reaction of zinc and lead foils with $AgNO_3$ solution. Silver dentritic nanostructures were formed on zinc foil (Fig. S5) while there only existed silver nanosheets on lead foil (Fig. S6). The formation of silver nanostructures is related not only to the reaction rates of these metals and $AgNO_3$ solution but also to the size, morphology and self-assembly mode of the silver nanoparticles formed during the reaction [17,18]. We will conduct in-depth research on this mechanism in subsequent studies.

Fig. 5 shows Raman spectra of Rhodamine 6G (R6G) solutions detected by different substrates [19]. For solid R6G [20] there is some intrinsic Raman peaks appear at 610, 771, 1197, 1366, 1504, 1538, 1575 and 1648 cm^{-1} (orange curve), while the intensity of the peaks is low. For the 10^{-5} mol/L R6G solutions on the rough silver foil, the intensity of the peaks is almost the same as solid R6G (light blue curve). But the intrinsic Raman peaks of R6G at 430, 610, 771, 918, 1197, 1307, 1366, 1504, 1538, 1575,

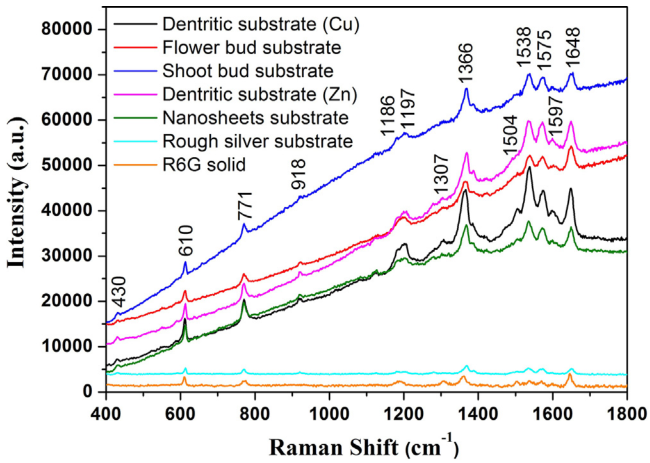

Fig. 5. Raman spectra of R6G solution on different SERS substrates and R6G solid.

1597, 1648 are all present (black curve) when silver dentritic nanostructures were used as SERS substrate. For the 10^{-5} mol/L R6G solutions on the flower bud (red curve) and shoot bud (blue curve) substrates, Raman peaks of R6G are all present but the intensity of the peaks is lower than that of silver dentritic nanostructure. Silver fractal nanostructures can, therefore, detect the complete set of Raman signals of R6G solution. The Raman spectra of p-Hydroxybenzoic acid (PHBA) solution on different SERS substrates are shown in Fig. S7. The substrates which have fine structures wound have better SERS effect. This result provides significant support on developing repeatable and stable trace detection technology of Raman spectrum. The performances of silver fractal nanostructures based on this preparation have guiding importance for the development and application of silver nanodevices.

4. Conclusion

Silver nanostructures with three kinds of fractal morphological characteristics were prepared by replacement reaction method and we find proper plants which have the same structure characters as them. These silver fractal nanostructures exhibit high SERS activity. The behavior of the SERS activity is consistent with a strong influence of the morphology of the fractal structures. The silver fractal nanostructures can significantly improve the detection sensitivity of SERS and have very important significance for trace analysis in chemistry [1], environment [3], medicine [7], and other fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.126808.

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