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Templateless Synthesis of Nanoporous Gold Sponge with Surface-enhanced Raman Scattering Activity

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We demonstrate templateless synthesis of nanoporous gold (Au) sponge by chemical reduction of Au species in aqueous solution. The obtained Au nanosponges exhibit surface-enhanced Raman scattering activity.

In the recent years, metal-based nanoporous materials have attracted a great deal of attention because of their various applications in various fields including electrocatalysis, photochemistry, sensing, and biofiltration. Different techniques for the production of various nanoporous materials have been developed so far. Among them, templated syntheses have been regarded as a general concept for making nanopores in metals. For example, by using colloidal crystals or other aggregated nanoparticles as templates, nanoporous metals with various compositions can be produced. By applying electrochemical processes with colloidal crystal templates, well-ordered nanoporous Au, Pt, Ni, Co, and metal oxide films have been reported.[1,2] Amphiphilic molecules such as surfactants can be also used as soft templates.[3–6] Ordered mesoporous metals can be realized by chemical reduction of metal species in the presence of lyotropic liquid crystals made of highly concentrated surfactants.[5] As other approaches for synthesis of nanoporous metals, biopolymer-assisted hydrothermal strategies[7] and dealloying[8–11] methods have been recently proposed. All of the previous methods, however, included complicated processes, and several steps and precise controls of synthetic parameters such as pH and temperature are required.

In this communication, we report templateless synthesis of nanoporous Au sponge by a rapid and one-step method at room temperature. Although very recently templateless synthesis using β-D-glucose was reported, the 12-h reaction period is too long, which is a serious problem for large-scale production.[12] The present method developed by us was shown to have high yield (ca. 100%), rapid synthesis rate, low cost, and capability of scale-up with simple equipment. Recent efforts have focused on the use of nanostructured Au as substrate for SERS.[13,14] Our nanoporous Au sponge consisting of interconnected nanowires showed excellent activity as suitable substrate for SERS. Furthermore, the sponge will be an active catalyst for carbon monoxide and NO_x oxidation in the future.

In this experiment, the starting precursor solutions were prepared by dissolving precise amounts of $HAuCl_4$ in water. The concentration of $HAuCl_4$ was varied from 1 to 20 mM. For the preparation of nanoporous Au sponge, 5 mL of $HAuCl_4$ solutions was mixed with 25 mL of sodium borohydride solution (40 mM). The mixtures were stirred for several minutes. After finishing the reaction, the deposited Au particles were agglomerated. The amount of reducing agents was sufficient to completely reduce all the Au species. Therefore, the solution colors were changed to transparent clear.

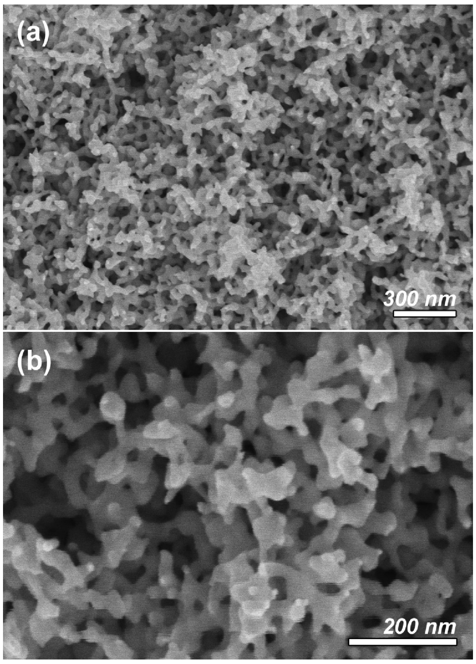

Figure 1. SEM images of nanoporous Au sponges prepared by using 10 mM $HAuCl_4$ solution. Figure (b) is highly magnified SEM image. The morphology of samples was observed with a Hitachi S-4800 field emission scanning electron microscope (FE-SEM).

Figure 1a showed the low-magnified SEM image of the nanoporous gold nanosponge prepared with 20 mM $HAuCl_4$ solution. The obtained samples showed bulk morphology with larger than 200 µm in size. In the deposited particles, several voids of a few micrometer size were formed (See Supporting Information, Figure S1.).[15] Since the reduction force of SBH is very strong, the SBH molecules released electrons by self-decomposition in the aqueous solutions. Therefore, a large amount of bubble of hydrogen gas was generated during the Au deposition, forming the voids with different sizes in the products. Higher magnified SEM image in Figure 1b shows that the Au nanowires are interconnected to make the macropores. The Au nanowires had many branches and the nanowire size was in the range of 10 to 30 nm. Close observation of these networks showed that pore sizes were not uniform. Additionally, the high-angle XRD diffraction showed the several peaks corresponding to Au fcc structure (not shown).

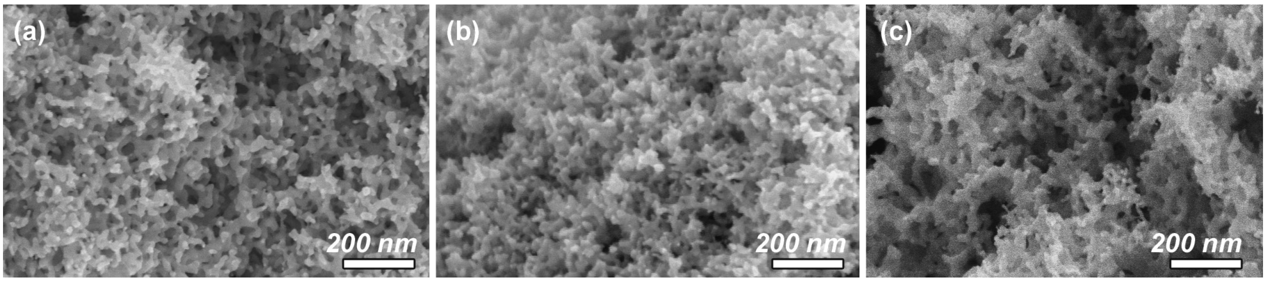

Figure 2. SEM images of nanoporous Au sponges prepared by using (a) 1, (b) 5, and (c) 20 mM $HAuCl_4$ solutions. The morphology of samples was observed with a Hitachi S-4800 field emission scanning electron microscope (FE-SEM).

Generally, SBH molecules spontaneously release lots of electrons by self-decomposition, so that metal species are reduced into metal immediately. By taking advantage of self-decomposition of SBH at low pH in aqueous solution, SBH has been widely used for the formation of fine nanoparticles.[16,17] The formation of nanostructured metals is highly dependent on the concentrations of the dissolved metal species. With increase of the concentrations of the metal species, the fine nanostructures such as nanoparticles are not easily formed. The similar situation was observed in the present system.

Figure 2 shows SEM images of the resultant products prepared under various concentrations of $HAuCl_4$ (the concentration of SBH was constant). As shown in Figure 2, well-defined nanosponges with the same morphology could be successfully produced in the range from 1 to 20 mM concentrations, and the branched shapes of the products also remained highly uniform in hyperbranched shapes. However, when the concentration of the $HAuCl_4$ was over 200 mM, micron-sized Au particles without any porous network were deposited. When the concentration of the Au species was much higher, lots of Au nuclei were immediately generated and then were gathered to form bluk irregular particles.

Recently, Au and Ag nanoparticles have been utilized as substrate for SERS applications. Large SERS enhancements can be achieved at particle junctions of the particle aggregates. It was previously reported that the aggregated nanoparticles showed superior SERS activity than isolated individual nanoparticles.[18] Because our nanoporous Au sponges possesses sufficient particle junctions, it is expected that they show excellent SERS activity. To investigate the SERS, Rhodamine B was used as the probe molecule. Rhodamine B (1.0 μM) was immobilized on the nanoporous Au sponges by drop casting. As a reference, a flat Au substrate without any nanostructures was used. As shown in Figure 3, the intensities of the SERS signals in nanoporous Au sponge were dramatically increased, which is attributed to the surface enhancement effect of the Au sponges. The peaks were clearly associated with Rhodamine B.[13]

In conclusion, we synthesized noble nanoporous Au sponges with high surface area by kinetically controlling the SBH reduction process. Our Au nanosponges will be good substrates for SERS applications. Also, our process can be simply extended to obtain nanosponges of other metals such as Ag, Pd, and Pt and alloys.

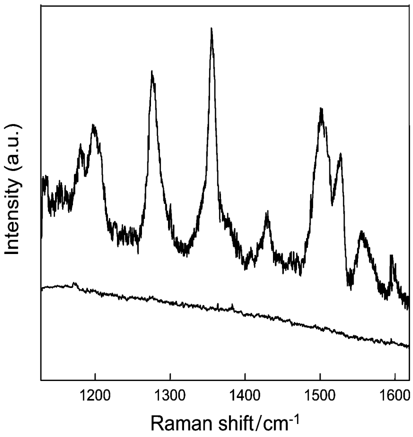

Figure 3. Raman spectra for Rhodamine B immobilized on (upper profile) the nanoporous Au sponge and (bottom profile) Flat Au substrate. The sample size is 25 mm^2 and the spot size is 1 μm. Micro-Raman scattering measurements were performed at room temperature with a 100× objective and a 532 nm excitation light. The excitation power was set to be about 0.2 mW.

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