EDTA-controlled One-pot Preparation of Novel Shaped Gold Microcrystals and Their Application in Surface-enhanced Raman Scattering

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We report a one-pot preparation method for a series of novel shaped gold microcrystals by simply mixing $HAuCl_4$ with disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA). Under the different reaction temperatures, spinous structures, multipod microspheres, and rough surfaced microspheres were obtained. These microcrystals exhibit high surface-enhanced Raman scattering (SERS) activity.

Metal colloids have attracted much attention because of their unique physical and chemical properties and important applications in optics, biology, and catalysis.[1] Morphology-controlled preparation of metal colloids is crucial challenge in nanoscience since the physicochemical properties of nanometer-scaled materials strongly depend on their shape and size besides their inherent chemical constitutions.[2] During the past decades, a variety of preparative methods of shape-controlled metal and semiconductor colloids have been developed. Particularly, special shaped gold colloids such as rods,[3] plates,[4] and polyhedron[5] have been prepared by using different wet-chemical methods. Recently, a number of groups have reported branched gold nanoparticles which attracted considerable attention.[6] All of these branched nanoparticles have rough surface features which are expected to have potential applications in surface-enhanced Raman scattering (SERS). In this letter, we report a one-pot method for the preparation of a series of rough surfaced gold crystals in submicrometer and micrometer sizes, which have novel shapes and larger size compared with the branched gold nanoparticles reported before.[6] In our study, for the first time, disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) acted as a reductive and shape-controlling reagent to make gold microcrystal with novel morphologies, while it was used as reducing reagent to prepare spherical silver nanoparticles previously.[7] The SERS activity of these rough surfaced microcrystals was evaluated using 4-aminothiophenol (4-ATP) and rhodamine 6G (R6G) as probe molecules. The results showed that these microcrystals exhibited high SERS activity.

In our experiment, 0.5 mL of 0.2 M Na_2EDTA was added to 1 mM $HAuCl_4$ solution with a 10:1 molar ratio of Na_2EDTA to $HAuCl_4$ at different temperature (25, 50, and 100 °C) under vigorous stirring. After completely reacted, some reddish brown precipitate was observed in the solution and on the surface of the vessel and stirrer.

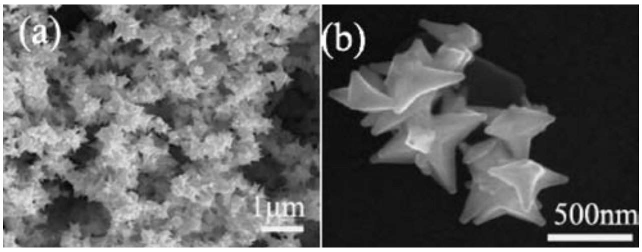

Figure 1. SEM images of (a) spinous structures and (b) star-shaped particles.

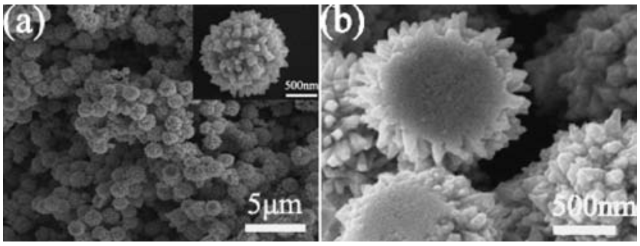

Figure 2. SEM images of (a) multipod microspheres and (b) multipod hemispherical particles. The inset in (a) is the high magnification SEM image of a single multipod microsphere.

Figure 1 shows the scanning electron microscopy (SEM) images of the precipitate obtained at 25 °C. Low magnification SEM image (Figure 1a) suggests the formation of micrometer-sized spinous structures with rough surfaces which consist of many branches in length of hundreds nanometers. X-ray diffraction (XRD) pattern confirms that the precipitate is face-centered cubic (fcc) gold (not shown). In addition to these disordered aggregated spinous structures, there are also many dispersed star-shaped particles (300–500 nm) (Figure 1b). The shape of each horn of the star-shaped particles is like a pyramid with the tip outward, which is the same as the "branches" of the spinous structures.

A typical SEM image of precipitate obtained at 50 °C is shown in Figure 2a. Multipod microspheres (ca. 1.5 μm) were obtained. In addition, some hemispherical particles (Figure 2b) could be found. It is supposed that they were formed on the surface of the vessel and dispersed in the solution by subsequent ultrasonic treatment, which agrees with the literature reported.[8] As shown in Figure 2b, dozens of "pods" in a mean length of 175 nm protuberating from a central solid sphere at different directions can be clearly observed.

As the reaction temperature is increased to 100 °C, rough surfaced microspheres (ca. 1 μm) are observed (Figure 3a). Compared with the multipod microspheres obtained at 50 °C, the protuberance becomes shorter and smaller. As shown in the high magnification SEM image (inset), the surfaces of the rough surfaced microspheres consist of many nanoparticles in a mean size of 77 nm. The result shows that the morphology of the products changes from aggregated structures to dispersed spheres and that the protuberance on the surface becomes shorter

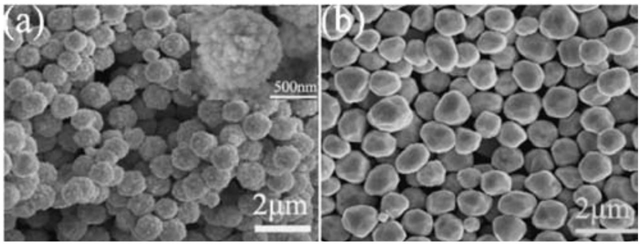

Figure 3. (a) SEM image of the rough surfaced microspheres. The inset is the surface feature of the rough surfaced microspheres. (b) SEM image of the faceted microcrystals.

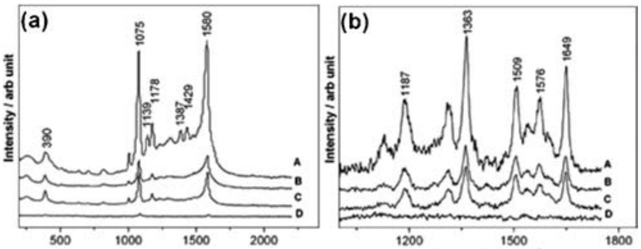

Figure 4. SERS spectra of (a) 4-ATP and (b) R6G adsorbed on (A) the rough surfaced microspheres, (B) the multipod microspheres, (C) the spinous structures and (D) the faceted microcrystals.

and smaller along with higher reaction temperatures. The same tendency is observed when the molar ratio of Na_2EDTA to $HAuCl_4$ is changed from 10:1 to 20:1. As a control experiment, we also prepared faceted gold microcrystals (ca. 1 μm) (Figure 3b) with much smoother surface using a modified polyol method.[9]

The SERS spectra (Figure 4) were measured with FT–Raman spectrometer (excitation wavelength at 1064 nm) and confocal microscopic Raman spectrometer (excitation wavelength at 514.5 nm) using 4-ATP (10^{-5} M) and R6G (10^{-5} M) as probe molecules, respectively. The faceted microcrystals exhibit very weak enhancement (curve D). As for multipod microspheres (curve B) and spinous structures (curve C), the SERS spectrum becomes stronger and the rough surfaced microspheres exhibit the strongest SERS spectrum (curve A), which is attributed to their unique surface features. The rough surfaced microspheres consisting of aggregated nanoparticles in a mean size of 77 nm is particularly efficient for SERS enhancement.[10] Moreover, the aggregation of nanoparticles[11] and the nanoscaled roughness[12] are also important factors contributing to SERS enhancement. Although the surfaces of multipod microspheres and spinous structures consisting of larger particles are supposed to exhibit depressed SERS activity, both of them show high SERS signals compared with the faceted microcrystals which is most likely caused by the lighting-rod effect of the similar protuberant tips on their surface.[13]

In summary, three kinds of gold microcrystals, the spinous structure, multipod microspheres, and rough surfaced microspheres, were prepared by simply mixing $HAuCl_4$ with Na_2EDTA under different temperatures, and all of them exhibit high SERS activity.

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