

Synthesis and characterization of gold nanodogbones by the seeded mediated growth method

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Nanotechnology, 18, 395603 (September, 2007)

In recent years, nanoparticles have continued to attract considerable attention in many scientific fields, such as material research, nano- and molecular electronics and technological applications. The size and shape of such nanoparticles are two important factors that determine their physical, chemical, optical, magnetic, catalytic and electronic properties. Therefore, effectively controlling their shape and size is very important, and is a challenging task for researchers.

Gold is well known to be the most important noble metal material due to its unique optical responses, and its catalytic, photographic, biosensing and electronic properties. It has been the subject of research and is applied widely in many fields such as surface-enhanced Raman scattering (SERS), optical sensors, fluorescence signals, molecular sensors, surface plasmon resonance (SPR) sensor chips, deoxyribonucleic acid (DNA) sensors and electrochemical sensors.

Recently, several shapes and structures of gold nanoparticles have been studied. They include nanorings, nanoplates, dendrimer-like shapes, nanocubes, nanoprisms, crooked nanorods, nanodumbbells and nanonetworks. The development of well controlled shapes and novel structures of gold nanoparticles has therefore become an emerging research topic. This material has also been synthesized by various methods which include the electrochemical method, laser ablation, the photochemical method, the sonochemical method and electrodeposition with a porous template membrane, among others. However, all of these methods have some disadvantages in practical use, such as high processing temperature, complexity, low growth ratio and expensive equipment. Thus, an economic and simple synthetic technique is necessary for the fabrication of gold nanoparticles.

Gold nanoparticles were prepared by the wet chemical reduction of gold salts in this work. A seeded mediated growth (SMG) method was used to make gold nanoparticles with highly uniform size and shape. The SMG method was found to be superior to other approaches for synthesizing gold nanoparticles because of its high quality, ease of control of the yield, low processing temperature, large amount synthesized, inexpensive equipment, high growth rate and low cost. In the SMG method, gold nanoparticles are produced in reasonable yield by chemically reducing HAuCl₄ in a surfactant solution, with the addition of small seed gold particles as nucleation centers for the preparation of large nanoparticles. The surfactant absorbs strongly (as a bilayer) along the crystal face of the nanoparticle. It is usually considered to be a soft micelle template, which controls the size and shape of the nanoparticles.

This work describes a SMG method that involves the addition of vitamin C solvent to prepare gold nanodogbones (GDBs). Vitamin C is found to modify the shape of gold nanoparticles from rod structures

to dogbone-like structures. The aspect ratio (R) of GDBs can be easily controlled by varying the amount of added vitamin C solvent. The R is defined as the ratio of average length to average diameter of a cylinder. This work focuses on the crystalline structure and optical properties of the GDBs.

Figure 1(a) shows the low-magnification TEM image of the gold seed, which is almost spherical and uniformly dispersed with a size of about 5 nm. Figure 1(b) shows a TEM image of gold nanoparticles at low magnification formed by the SMG method without addition of vitamin C solvent: they are shaped like rods. A higher-magnification TEM image of the gold nanorods in the inset in figure 1(b) yields an estimated rod length of 20–30 nm and a diameter (width) of 8–15 nm. Figures 1(c)–(f) show the TEM images of gold nanoparticles formed by the SMG method with the addition of 10, 20, 30 and 40 μ l of vitamin C solvent. The experimental results clearly indicate that the shape of the particles can be changed by altering the amount of vitamin C solvent. When the amount of vitamin C solvent is 10 μ l, many highly uniform gold nanoparticles, which are almost GDBs, are formed, as shown in Figure 1(c). These GDBs have fatter ends and thinner middle sections. The vitamin C solvent may act as a shape modifier from rod-like to dogbone-like. As the amount of vitamin C solvent is increased in the range from 20 to 30 μ l, the length of the GDB is decreased, as shown in figures 1(d), (e). When the amount of vitamin C solvent is 40 μ l, the gold nanoparticles are spherical, with rough and irregular structures, such as twisted gold nanospheres (TGNSs), as shown in Figure 1(f). However, the length of the GDB decreases as the amount of vitamin C solvent increases, and the particle shape can also be changed from GDB to TGNS.

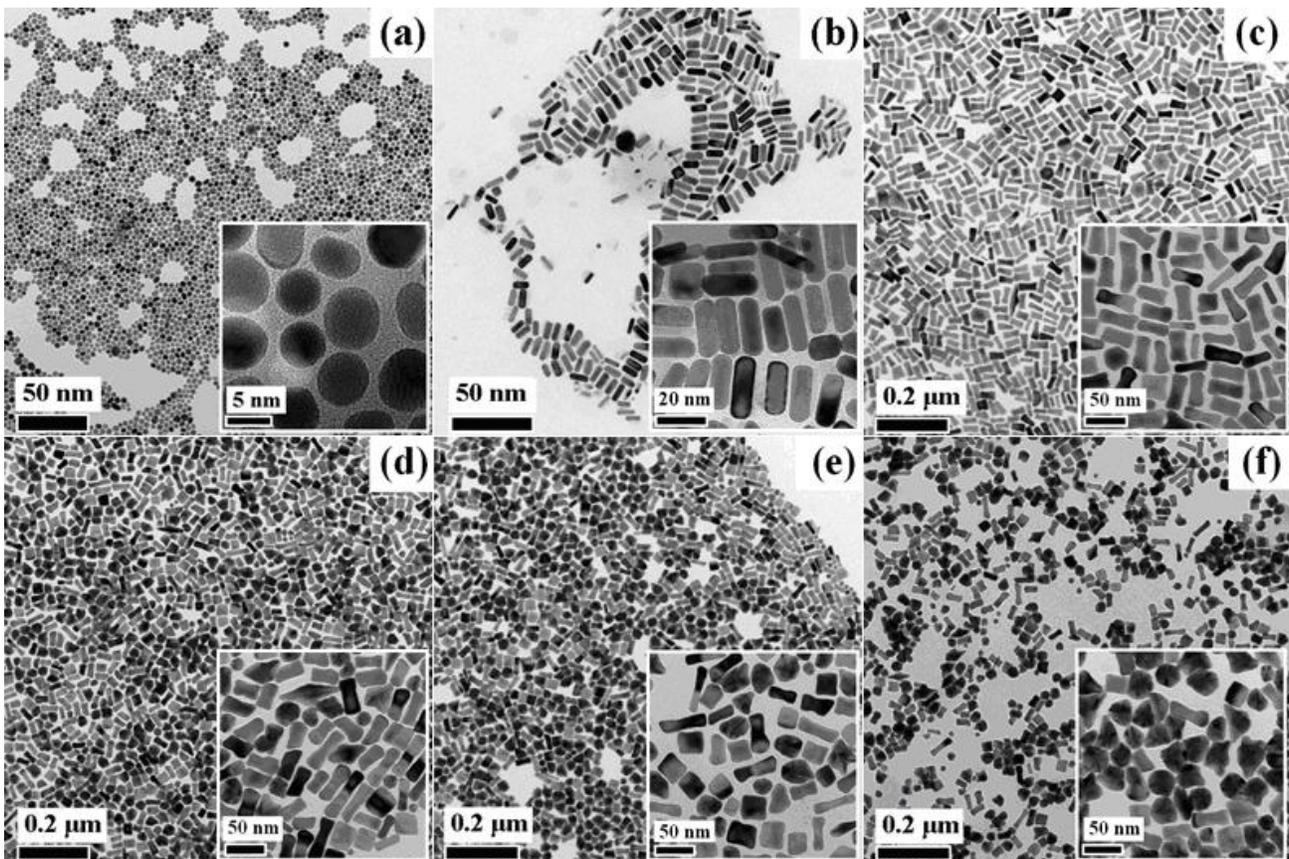


Figure 1. (a) TEM images of the gold seed particles with spherical shape. (b) TEM image of the gold nanorods without additional vitamin C solvent by the SMG method. (c)–(f) TEM images of the GDBs with 10, 20, 30 and 40 μ l of additional vitamin C solvent by the SMG method.

Figure 2 displays the shape-dependent UV–NIR absorption spectra of the gold nanoparticles with different aspect ratio (R), as determined by the SMG method. When a gold seed solution was used, the optical response of the spherical gold seed exhibits a single SPR band at around 520 nm, as shown in curve (a) of Figure 2. Curve (b) of Figure 2 shows a UV–NIR absorption spectrum of gold nanorods without additional vitamin C solvent. Rod-shaped gold particles generally have two SPR absorption bands that are characteristic of the long and short axes of the rods; one peak corresponds to the short axes (transverse dipole resonance) and appears at a shorter wavelength of around 520 nm, while the other corresponds to the long axes (longitudinal dipole resonance) and appears at a longer wavelength of around 600–1300 nm, depending on R . This sample of gold nanorods, with R of 2.34, shows the transverse SPR band at 522 nm and a longitudinal SPR band at 823 nm. The addition of vitamin C solvent to the growth solution changes the absorption spectra in an amount-dependent manner. Curves (c)–(f) of figure 2 show the UV–NIR absorption spectra of the GDBs with different amounts of additional vitamin C solvent. The blue shift in the longitudinal SPR band from 713 to 676 nm was observed as the shapes of the gold particle changed from GDB to TGNS as the amount of vitamin C solvent varied in the range 10–40 μ l. In our experimental study, the longitudinal SPR band of the GDBs was similar to that of normal gold nanorods, depending on R .

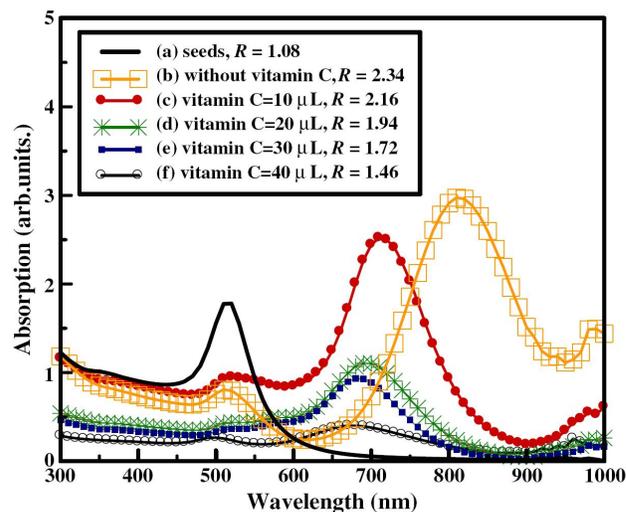


Figure 2. UV–NIR absorption spectra of GDBs prepared under various reaction conditions, as a function of vitamin C amount.

Figure 3(a) shows the TEM image of a single GDB by the SMG method with the addition of vitamin C. The high resolution transmission electron microscopy (HRTEM) image in the inset of Figure 3(a) shows that the GDB are single crystals with no observable stacking faults or twins defect. The fringe spacing is measured to be 0.232 nm, which corresponds closely with the spacing between the (111) planes of fcc gold (0.235 nm). Figure 3(b) shows an electron beam that is perpendicular to the facets of individual GDBs. The characteristic spot array in the diffraction pattern of a single crystal confirmed that the GDBs were single crystals, which result is consistent with HRTEM analysis. The lattice constant calculated from this selected-area electron diffraction (SAED) pattern is 4.063 Å, which agrees with a reported value for the fcc lattice gold phase ($a = 4.078$ Å; JCPDS 04-0784). Figures 3(c) and (d) show the bright-field (BF) TEM image of a single GDB and the corresponding dark-field (DF) TEM image. DF TEM image analysis, as in Figure 3(d), determined that this contrast arises from thickness fringes oriented for strong Bragg scattering. The thickness fringes exhibiting strong diffraction contrast are simultaneously visible as ring patterns and bright regions in the GDB surface.

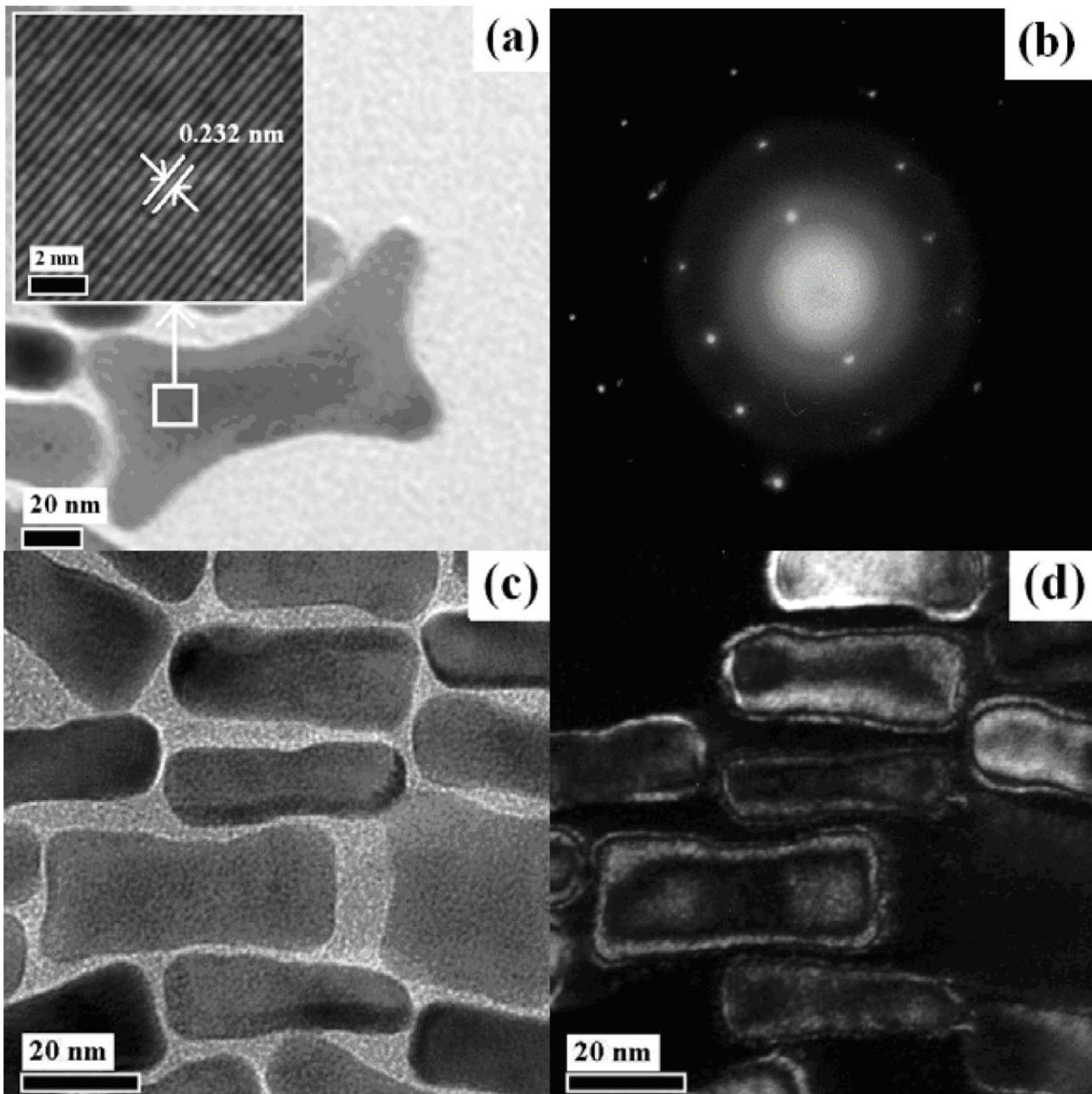


Figure 3. (a) TEM image of the single GDB. (b) The corresponding SAED pattern was obtained by directing the incident electron beam perpendicular to one face of the GDB. (c) Bright-field TEM image of GDB and (d) the corresponding dark-field TEM image.