

## LETTERS

### How Does a Gold Nanorod Melt?#

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Structural transformation of gold nanorods are investigated by high-resolution transmission electron microscopy after they have been exposed to low-energy femtosecond and nanosecond laser pulses in colloidal solution. The pulse energies were below the gold nanorod melting threshold, but allowed early stage shape transformation processes. It is found that while the as-prepared nanorods are defect-free, laser-irradiation induces point and line defects. The defects are dominated by (multiple) twins and stacking faults (planar defects), which are the precursor that drives the nanorods to convert their {110} facets into the more stable {100} and {111} facets and hence minimize their surface energy. These observations suggest that short-laser pulsed photothermal melting begins with the creation of defects inside the nanorods followed by surface reconstruction and diffusion, in contrast with the thermal melting of the rods or the bulk material, where the melting starts at the surface.

#### Introduction

Due to their potential technological applications, the synthesis and study of the properties of nanoparticles has been a very active field of research.<sup>1–6</sup> One of the many chemical and physical preparation methods of metallic nanoparticles is the production of nanoparticles by laser ablation.<sup>7–11</sup> Recently, the treatment of already-prepared nanoparticles with laser light has been of great interest since it was found that it is possible to change the particle size and shape after preparation.<sup>12–24</sup> The laser light can serve as a convenient tool to control the size and shape distribution of an often inhomogeneous nanoparticle sample. In several studies, fragmentation and melting of gold and silver nanoparticles of different shapes supported on a quartz substrate,<sup>12,13</sup> in a glass matrix,<sup>14,15</sup> and in colloidal solution<sup>16–24</sup>

have been reported. The size and shape distribution of the final irradiation product is found to depend on the pulse energy,<sup>16–19,21,22</sup> laser wavelength,<sup>12,13,19,20</sup> and pulse width.<sup>21,22</sup>

It is known that the melting of the nanoparticles starts at their surfaces at reduced temperatures.<sup>25,26</sup> The surface melting of metallic nanoparticles can directly be studied by in-situ transmission electron microscopy (TEM) as has been reported recently for gold<sup>27</sup> and platinum<sup>28</sup> nanoparticles of nonspherical shape. In general, transmission electron microscopy (TEM) is a powerful technique to analyze the structure of nanoparticles<sup>29–33</sup> as well as their melting behavior.<sup>34–36</sup> In most studies on the melting of nanoparticles, the particles and the host medium were both in direct contact with a temperature source. On the other hand, the laser light selectively excites the metallic nanoparticles homogeneously without direct heating of the particle environment. Although it has been shown that a surface melting of colloidal gold nanorods into shorter and wider rods is also possible when using low-energy femtosecond pulses,<sup>22</sup> indicating a diffusion of surface atoms and a surface premelting, it is of interest to study the atomic rearrangements in more detail in

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# The word *melting* in this paper is used to describe the conformational change of the nanorod to the nanosphere as the experiments used do not actually observe the melting state itself, if it is present.

order to gain insight into the mechanism of the structural rod-to-sphere shape transformation.

In this communication we report the results of high-resolution TEM (HRTEM) studies on gold nanorods after exposure to femtosecond and nanosecond laser pulses with low pulse energies. The pulse energy is below the energy threshold required for a complete melting of the gold nanorods at which only an optical hole burning within the broad absorption band of the longitudinal surface plasmon resonance is observed.<sup>21–23</sup> It is found that the structural rearrangements of the gold atoms for the rod-to-sphere transition starts in the interior of the rod by the creation of point and line defects which then evolve into planar defects (e.g., stacking faults and (multiple) twins). A model for the structural transition from a nanorod to a spherical nanoparticle (nanodot) is proposed.

### Experimental Section

The preparation and procedure for the laser irradiation experiments have been described in detail elsewhere.<sup>21–23</sup> Briefly, the gold nanorods were prepared by electrolysis<sup>37</sup> in an aqueous solution consisting of a mixture of tetraalkylammonium bromide salts, which act as the electrolyte and form rodlike micelles. The laser sources used for the irradiation of the colloidal gold nanorod solution were an amplified Ti–Sapphire laser system (Clark MXR, CPA 1000) producing 100 fs pulses and an optical parametric oscillator (Spectra Physics, MOPO-730) producing pulses with a duration of 7 ns. The pulse energy was attenuated by neutral density filters, and the exposure time was controlled by a shutter. For the experiments reported here both lasers were set to a wavelength of 800 nm, which corresponds to the fundamental of the femtosecond laser and the idler of the nanosecond optical parametric oscillator.

The TEM sample was prepared by dispersing a droplet of the colloidal solution onto a thin carbon film supported by a copper grid. The structure of the nanoparticles was analyzed by high-resolution TEM at 400 kV using a JEOL 4000EX at a point-to-point image resolution of 0.18 nm.

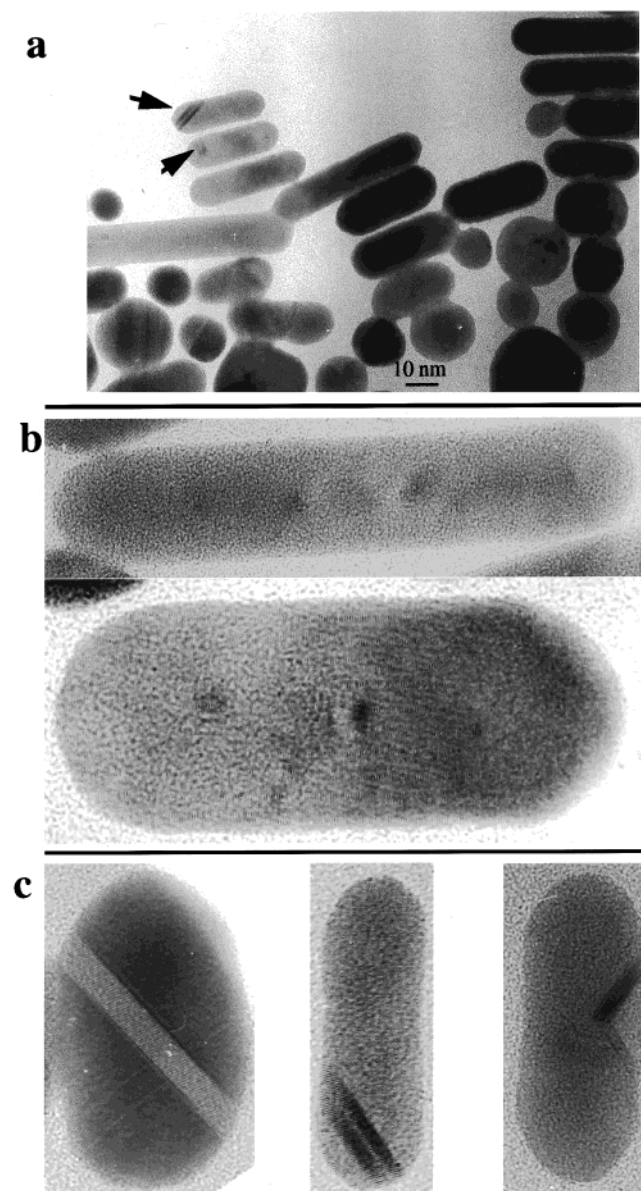
### Results and Discussion

We have reported previously<sup>21–23</sup> that gold nanorods prepared electrochemically and suspended in aqueous solution can be transformed into near-spherical nanoparticles of comparable volumes by the use of femtosecond laser pulses. The excitation of the nanorods with short laser pulses leads to the heating of the lattice of the nanorods in 1–4 ps by electron–phonon relaxation.<sup>38–42</sup> It can be assumed that the gold nanorods are uniformly heated since irradiation at 800 nm leads to the collective excitation of all the conduction electrons due to the longitudinal surface plasmon resonance. The thermal equilibration of the excited electrons is on the order of tens to hundreds of femtoseconds leading to a uniformly heated electron gas of the nanorod, which then couples with the lattice phonons. As the particles reach their melting temperature, they undergo a shape transformation to the thermodynamically more stable shape (i.e., spherical shape). The melting of a gold nanorod was found to take place in about 30 ps.<sup>24</sup> This time is shorter than the time found to cool off the hot lattice.<sup>40,42</sup> Furthermore, it was demonstrated that the laser-induced melting of colloidal nanorods is more gentle and more efficient with femtosecond laser pulses than with the longer nanosecond pulses.<sup>22</sup> Particularly, the energy of the femtosecond pulses can easily be controlled so that no simultaneous fragmentation of the nanorods takes place.

We also have reported on the structure of colloidal gold nanorods prepared electrochemically as well as the nanodots obtained after photothermal melting of the nanorods.<sup>43</sup> It was found that short nanorods with aspect ratios of 3–7 have the {100}, {111}, and {110} facets and contain no volume dislocations, stacking faults, or twins. The relatively unstable {110} facet is, however, absent in the spherical-like nanodots prepared by photothermal melting of the nanorods. The nanodots are dominated by {111} and {100} facets with shapes of truncated octahedral, icosahedral, and decahedral. The {111} and {100} facets are the lower-energy faces of gold. To reduce the strain associated with the spherical-like particle shape and to accommodate the presence of only {111} and {100}, the nanodots must contain planar defects. It is in fact well-known that there are planar defects such as twins and stacking faults present in spherical-like gold nanoparticles regardless of their method of preparation.<sup>29–33</sup> An example of a multiple twinned particle is an icosahedral which consists of 20 tetrahedra with {111} facets.<sup>29</sup>

To better understand the nanorod-to-nanodot shape transformation on a nanometer scale we exposed colloidal gold nanorods to laser pulses with pulse energies below the threshold needed for a complete melting of the nanorods and followed the changes in their structure by use of HRTEM. Figure 1 shows HRTEM images of gold nanorods after exposure to femtosecond laser pulses with a fluence of  $1 \text{ mJ cm}^{-2}$  ( $0.5 \mu\text{J}$  per pulse focused to a spot size of roughly  $250 \mu\text{m}$ ). This pulse energy is below the threshold required for a complete melting of the nanorods into near-spherical nanoparticles. Based on the degree of structural transformation observed in the TEM images for the exposed gold nanorods, different particles within the wide size distribution have absorbed different amounts of laser energy. Intermediate particle structures, such as bent, twisted, or  $\phi$ -shaped particles, can be observed in the irradiation product.<sup>22</sup> The nanorods show point defects and twins as indicated by the arrowheads in Figure 1a. The point defects and twins are more clearly seen after further enlargement of individual particles in Figures 1b and 1c, respectively. A similar result is found after exposure of the colloidal gold nanorods to nanosecond laser pulses with a fluence of  $250 \text{ mJ cm}^{-2}$  ( $20 \mu\text{J}$  per pulse, spot size of about  $100 \mu\text{m}$ ). Figure 2a,b shows nanorods with stacking faults and twinned particles after exposure to nanosecond laser pulses, respectively.

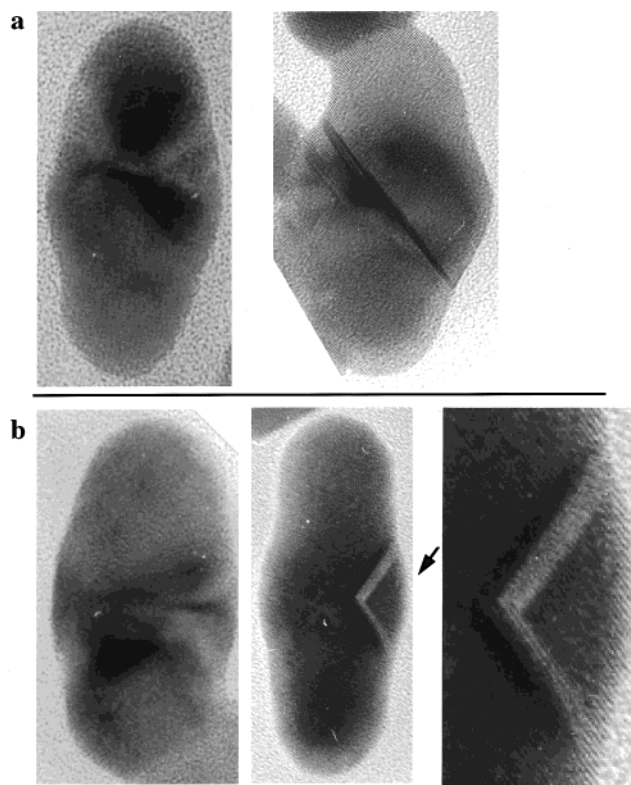
Since the types of defect structures seen in the exposed nanorods are also present in the nanodots prepared by photothermal melting of nanorods but are absent in the electrochemically as-prepared nanorods without laser irradiation,<sup>43</sup> it can be concluded that rearrangements of the gold atoms for the rod-to-sphere transition starts in the interior of the rod by the creation of point and line defects which then evolve into planar defects (e.g., stacking faults and (multiple) twins). From the above discussion, it is clear that the presence of defects is necessary for the shape transformation of nanorods into spherical-like nanoparticles. It is therefore thought that the laser-induced structural shape changes start around point defects as nucleation centers, which are found in the interior of the nanorods. Hence, the photothermal laser melting of nanorods starts within the nanorods, which is in contrast to the melting of bulk materials where the melting starts at the surface of the substrate. On the other hand, surface diffusion induced by laser irradiation led to the change in particle shape, as observed in Figure 1. Therefore, a surface premelting was concluded from the fact that mainly shorter and wider nanorods were found when this gold nanorod solution was exposed to



**Figure 1.** (a) HRTEM image of gold nanorods after exposure to femtosecond laser pulses with a fluence of  $1 \text{ mJ cm}^{-2}$  ( $0.5 \mu\text{J}$  per pulse). The nanorods show point defects and twins as indicated by arrowheads in (a). This is more clearly seen after further photographic enlargement of individual particles in (b) and (c). (b) shows two examples of nanorods with point defects, while (c) shows three twinned particles.

$1 \text{ mJ cm}^{-2}$  femtosecond laser pulses and then analyzed by TEM. The statistical analysis of the size and shape distribution of the nanorods before and after laser exposure is presented elsewhere.<sup>22</sup>

Figure 3 illustrates a proposed mechanism of the rod-to-sphere shape transformation process. The as-prepared nanorods are defect-free single crystals. The sides of the rod are enclosed by  $\{110\}$  and  $\{100\}$  facets, and its growth direction is  $[001]$  (Figure 3a). The small  $\{111\}$  facets are present but only at the corners. While being illuminated by pulsed laser light, point defects are first created in the body of the nanorods (Figure 3b), which serve as the nuclei for the formation of twins and stacking faults (Figure 3c). The twin is formed by two crystals with a specific orientation, and it is possible only if local melting occurs. This suggests that the melting first takes place at the defect sites in order to form a twinned crystal. Then, surface diffusion must take place simultaneously in order to enhance the growth of



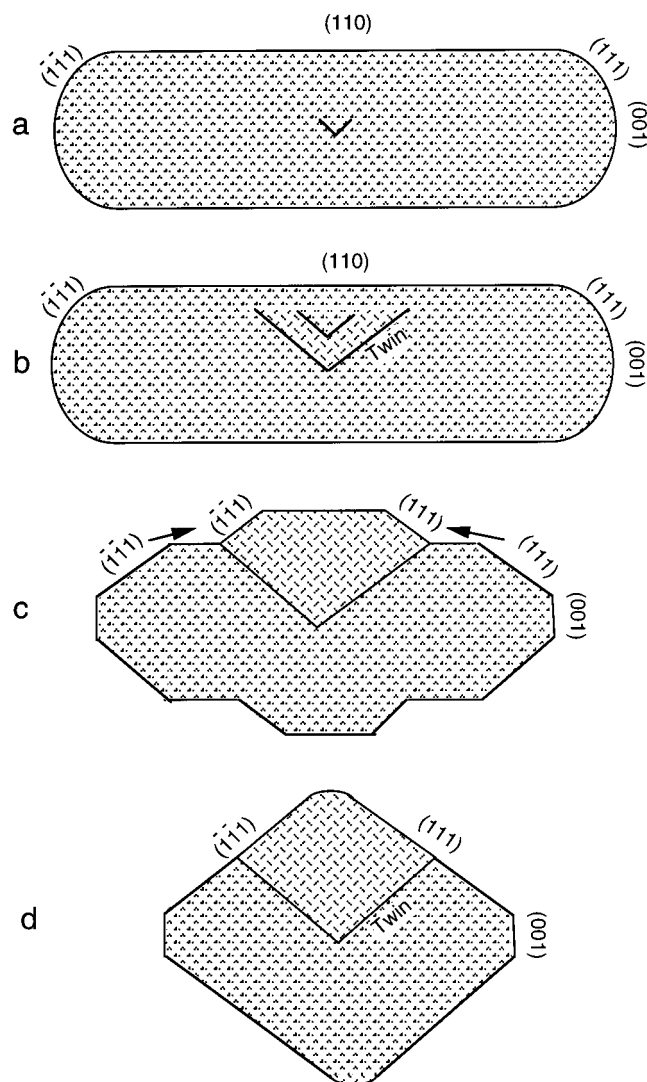
**Figure 2.** HRTEM image of gold nanorods after exposure to nanosecond laser pulses with a fluence of  $250 \text{ mJ cm}^{-2}$  ( $20 \mu\text{J}$  per pulse). (a) shows nanorods with stacking faults and (b) twinned particles. Similar defect structures are found in spherical gold nanoparticles after complete shape transformation nanorods while the as-prepared nanorods are found to be defect free.<sup>43</sup>

the twinned crystal (Figure 3d). This is driven by reducing the surface energy by reducing the  $\{110\}$  surface area and increasing the  $\{111\}$  surface. A continuation growth of the twinned crystal finally eliminates the unstable  $\{110\}$  surface, and the entire particles are enclosed by the more stable  $\{111\}$  and/or  $\{100\}$  faces (Figure 3e).

In conclusion, high-resolution TEM revealed that point and planar defects are present in gold nanorods after laser irradiation although the as-prepared nanorods are defect-free. The defects are dominated by (multiple) twins and stacking faults (planar defects), which are the precursor that drives the nanorods to convert their  $\{110\}$  facets into the more stable  $\{100\}$  and  $\{111\}$  facets. It is suggested that the shape transformation in the pulsed laser photothermal heating begins with the creation of defects within the nanorods body, at which local melting may occur almost simultaneously with surface premelting (diffusion). This is in contrast to the equilibrium thermal melting of bulk materials or shaped nanoparticles, e.g., gold nanorods<sup>27</sup> or platinum tetrahedra.<sup>28</sup> In these cases melting starts at the surface.

The above observation regarding the difference in the melting behavior may result from the difference in the mode of heating and cooling of the two cases. In thermal heating, it is heating under near equilibrium conditions. Due to the fact the surface atoms are less stable, they give rise to surface melting. In pulsed laser photothermal heating, the electron-phonon relaxation rapidly heats the gold nanorod near homogeneously (the wavelength of the excitation light is 10 times greater than the nanorod size), but cooling of the surface atoms is faster than the body atoms. This leads to temperature gradients with the initial construction occurring first in the middle of the nanorod.





**Figure 3.** A schematic process for the structural transformation from nanorod to nanodot.

This probably occurs in less than 30 ps (the measured melting time of the gold nanorods).<sup>24</sup>

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