

Supporting Information

The Fragmentation of Gold Nanoparticles Induced by Small Biomolecules

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Generally, nanoparticles injected by electrons should yield a blue shift rather a red shift in UV-vis spectra.¹ We believe that the red shift should be ascribed to two factors. First, hydrogen bonding induces the assembly of the gold particles. Cysteine is water soluble and would readily bind to the surface of gold nanoparticles via a thiolate linkage. Thus, -NH₂ group and its adjacent carboxylic acid group will project from the nanoparticle surfaces (Scheme 1B).² The intermolecular hydrogen bonding between the cysteine molecules located on different gold nanoparticles is beneficial to induce the assembly of gold nanoparticles.³ During the nanoparticles fragmentation, these fragments are easily

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linked onto large nanoparticles by intermolecular hydrogen bonding, which will lead to a red shift of the plasmon absorption band.⁴ Second, the red shift may be related with the distribution of surface charges on the nanoparticles. The gold atoms on nanoparticle surfaces are coordinatively unsaturated. Considering the R-SH is a strong nucleophilic reagent,⁵ the cysteine adsorbed on gold nanoparticles can donate an electron pair into unoccupied orbitals of gold existed on the surface.⁶ It has been reported that a surface gold atom carrying a nucleophilic molecule acquires a small positive charge δ^+ and the interior of the colloidal particles receives a corresponding negative charge δ^- .⁷ The $\delta^+\delta^-$ dipolar structure in gold particles causes a red shift in surface plasmon peak.⁸ When a large nanoparticles fragmentate into some small particles, the resulted fragments possess more surface gold atoms. As a result, there is an increase in the numbers of $\delta^+\delta^-$ dipolar structure. Therefore, the gold colloid suspension exhibits slightly red shifts during the fragmentating process of gold nanoparticles.

For the faded gold nanoparticles suspension, after diluting, a visible peak near to 250 was clearly observed (Figure S3). Considering the FT-IR spectroscopy and EI mass spectra experiments (shown in original manuscript), it is clear that the cysteine is formed, accompanying with the gold nanoparticles fragmentation.

Obviously, the concentration of cysteine in suspension has influence on the number of electrons injected into nanoparticles. Consequently, the gold nanoparticles fragmentation is dependent on the molar ratio of cysteine/Au, which is studied by adding different amounts of cysteine with the molar ratio of

cysteine/Au varied from 1:1, 8:1, 20:1, 40:1, to 120:1, while the HAuCl_4 concentration is kept constant at ~ 0.45 mM. At or above the ratio 40:1, the gold colloid suspension was entirely faded, indicating all of the parent gold nanoparticles fragmented into ultrasmall particles. At two lower molar ratios of 8:1 and 20:1, large nanoparticles were coexistent with ultrasmall particles, and the color of the gold colloid suspension became weak. When the molar ratio was reduced to 1:1, no fragmentation of gold nanoparticles was observed, which is consistent with previous reports about fabricating cysteine-capped gold nanoparticles.² In this case, only a certain number of cysteine molecules are chemisorbed onto gold nanoparticles surfaces. The charges inside gold nanoparticles are far less than the critical value of fragmenting nanoparticles. Thus, no gold nanoparticles are fragmented. At higher cysteine concentration, a majority of cysteine molecules are freely dispersed in colloid suspension besides chemisorbed cysteine. A large number of electrons are injected into gold nanoparticles because of the cysteine oxidation. Some nanoparticles with charges accumulated cross the Rayleigh threshold, which induce the gold nanoparticles fragmentation. Further increasing the concentration of cysteine will inject more electrons into gold nanoparticles. As a result, the initial gold nanoparticles will fragmentate into smaller particles. If the molar ratio of cysteine/Au up to 120:1, after the gold colloid suspension was faded entirely, the fragments of nanoparticles cannot be imaged by TEM due to their extremely small size, indicating the formation of atomic gold clusters.⁹ The result suggests that the size of nanoparticle

fragments can be controlled by cysteine amount.

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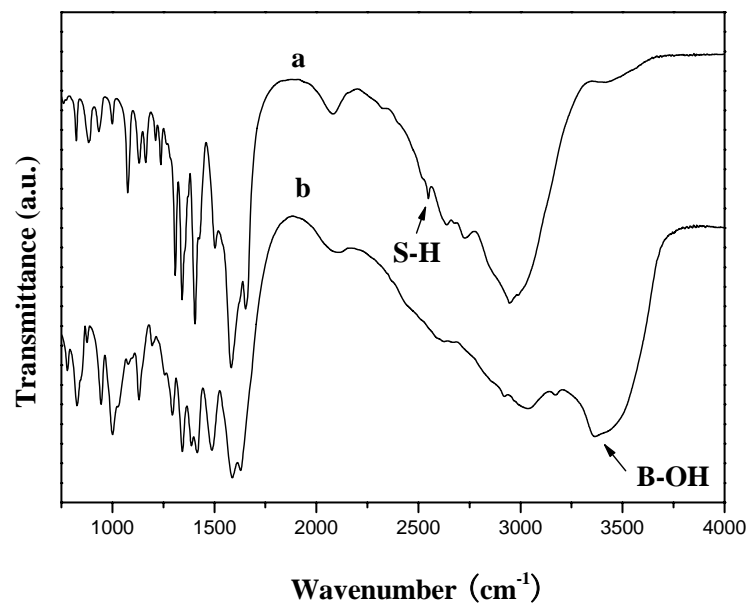


Figure S1. FT-IR spectra of pure cysteine (a) and gold colloid suspension in the presence of cysteine (b).

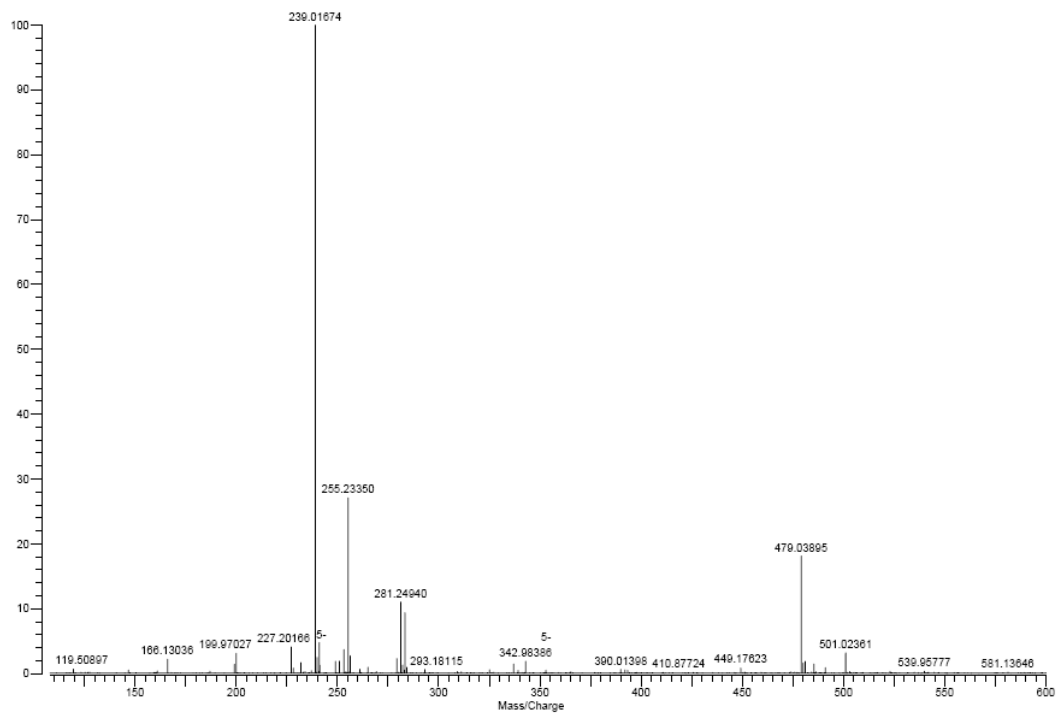


Figure S2. EI spectrum of cysteine in the gold nanoparticle fragments.

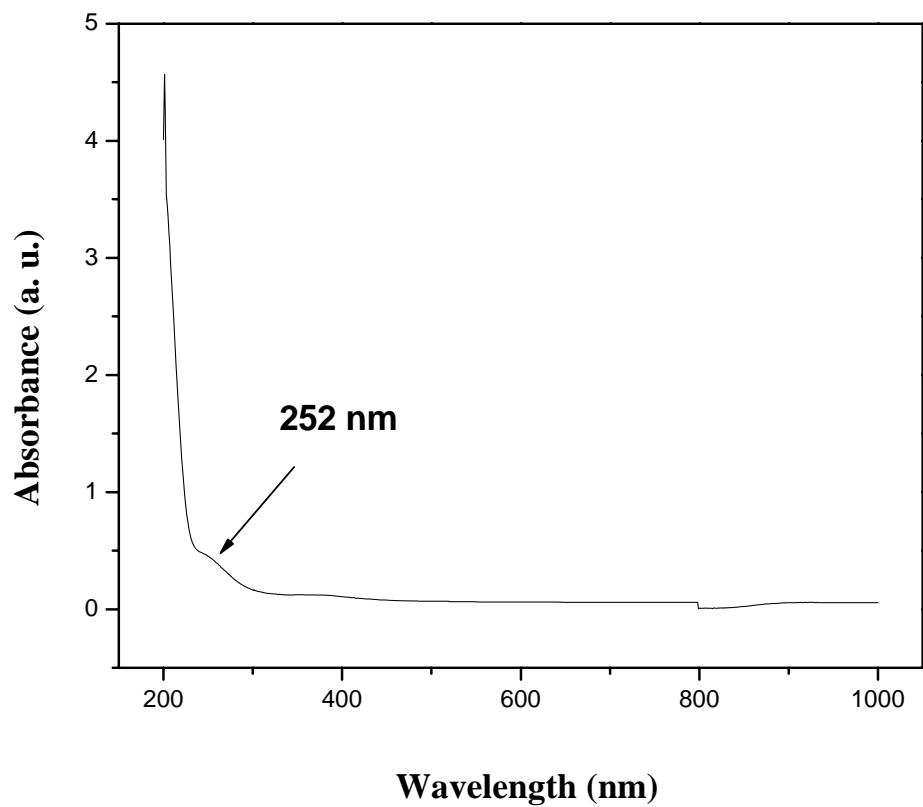


Figure S3. UV-vis spectrum of the faded gold nanoparticles suspension.

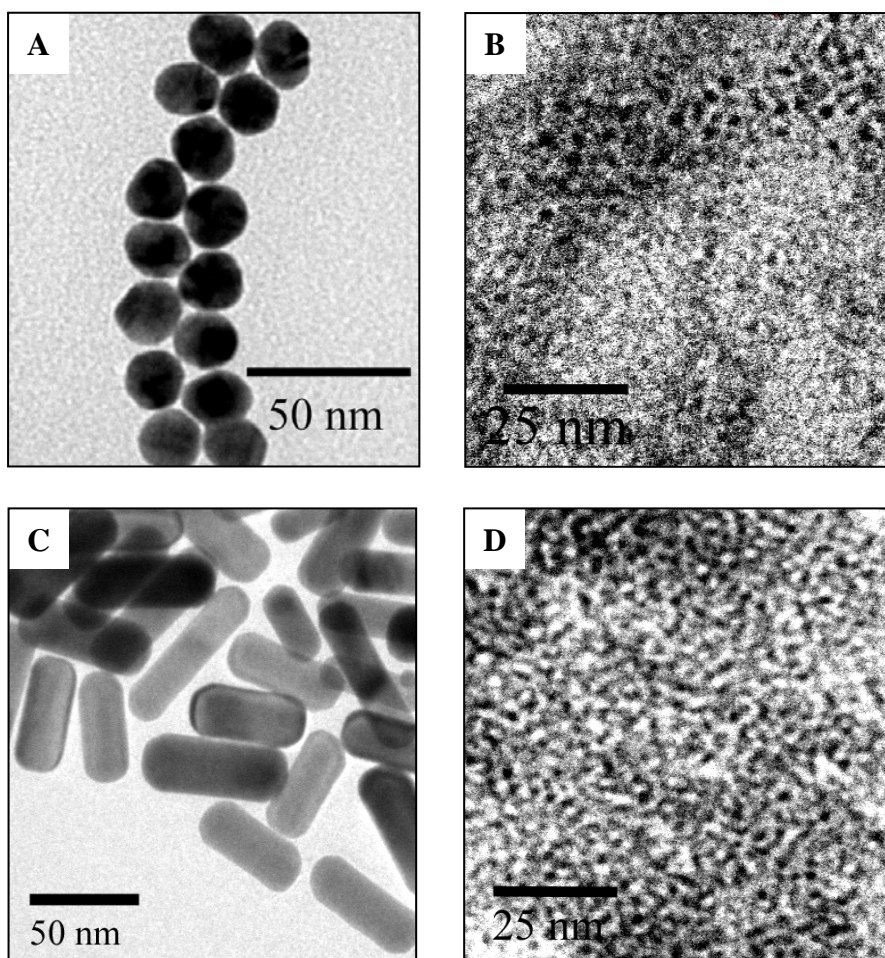


Figure S3. TEM images of (A) ~20 nm gold nanoparticles as well as (B) fragments, (C) gold nanorods and (D) corresponding fragments.