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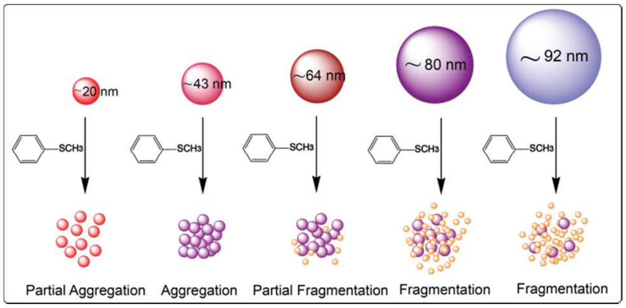

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COMMUNICATION

Thioanisole Induced Size-Selective Fragmentation of Gold Nanoparticles

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In this work, we report the features of size-selective fragmentation of gold nanoparticles (AuNPs) by thioanisole. Large particles are observed as prone to easier fragmentation than the smaller ones, the key-role being played by the effect of surface charge and surface coverage.

The thiols and dithiols are well known to have strong chemisorptions for gold surfaces through Au-thiol interaction as a result of which they could successfully passivate the gold nanoparticles (AuNPs) surface and increase their stability.[1,2] However, this perspective has been changed recently, since researchers found that thiols could also fragment the AuNPs to form atomic gold clusters.[3,4] The mechanism of this size-reduction of AuNPs has been extensively reported, however, one of the most widely accepted mechanism is the fragmentation of nanoparticles (NPs) by Coulomb explosion of surface charges. The electron injection by some nucleophilic reagent to the surface of the NPs may increase the charge density and according to Mafune *et al*, these highly charged AuNPs are electronically unstable and could undergo explosion by Coulomb repulsive forces.[5] This explosion by surface charges may lead to the fragmentation of NPs.

Previously, we have demonstrated the fragmentation of AuNPs (*ca.* 20 nm) induced by thiol derivative of ubiquinone, which involves the energetic electron injection from thiol-ubiquinone to AuNPs.[4] However, size-dependent fragmentation of the nanoparticles has not yet been explored. Continuing these efforts, in this work we further investigated that AuNPs size plays a pivotal role in how AuNPs behave toward their fragmentation by thioanisole. As the thioanisole is the methyl derivative of a long-familiar Raman marker, thiophenol, it could bind strongly to the surface of AuNPs; therefore, it is of particular interest to be investigated by surface-enhanced Raman spectroscopy (SERS) measurements. To the best of our knowledge, this is the first such study discussing the spontaneous size-selective fragmentation of the AuNPs under ambient conditions. Fig. 1 showed the schematic illustration for the change in AuNPs morphology after addition of thioanisole in different AuNPs solutions, representing that increasing the size of NPs makes them more susceptible to fragmentation, being affected by surface coverage and surface charges. In this work, apart from the visual appearances of the NPs solutions, UV-Vis and SERS spectra were employed to monitor the process of size-evolution/fragmentation followed by finally determining the morphology of AuNPs by HR-TEM.

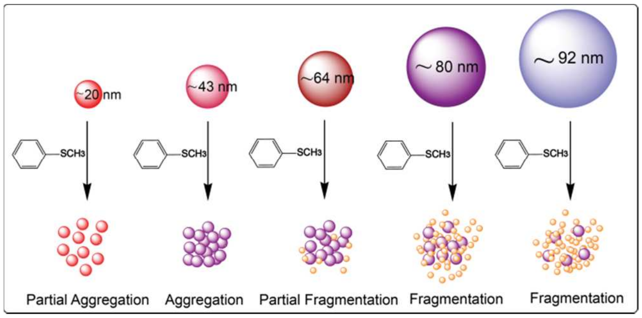

Fig. 1 Schematic Illustration of the effect of particles size on the fragmentation phenomenon of colloidal AuNPs assisted by thioanisole. The diameters shown may not match the exact proportions of NPs dimensions.

The absorption spectra of representative unaggregated colloids of different diameters are shown in Fig. 2A and their characteristic λ_{max} at 521 nm, 528 nm, 536 nm, 546 nm, and 558 nm were found in good agreement with literature data for *ca.* 20.1 nm, 42.9 nm, 63.9 nm, 80.4 nm, and 92.3 nm, respectively[6] (all values are mean diameters, see Table S1). The addition of thioanisole into aqueous solutions of different Au colloids resulted in diverse visual color changes for different particles sizes. Upon addition of thioanisole, the wine red color of the *ca.* 20.1 nm diameter AuNPs remained unchanged or slightly changed after a long time whereas for larger NPs, the colors of the solutions were immediately changed to purple/light purple and finally to colorless, representing the sequential processes of AuNPs aggregation or aggregation followed by fragmentation depending upon the size of NPs. It could be clearly observed that the same concentration of thioanisole generated significantly different enhanced SERS signals for Au colloids of different sizes with largest absolute SERS signal provided by *ca.* 42.9 nm diameter particles recorded 5 min later, after addition of thioanisole (Fig. 2B).

It is obvious from spectra in Fig. 3A that addition of 1 mM thioanisole gives loss of UV-Vis peak intensity and growth of some new features with a slight red shift of original absorption peak which also indicated the chemisorption of the compound onto the surface of the NPs.[7] However, with NPs of different sizes, the decrease in intensity was significantly altered. For smallest particles size in our experiment, *i.e.*, 20.1 nm, the time-resolved UV-Vis spectra showed a decrease in intensity for some specific intervals of time (Fig. 3A-a) until there was no further change in the intensity. The corresponding SERS spectra (Fig. 3B-a) initially did not show any obvious SERS enhancements due

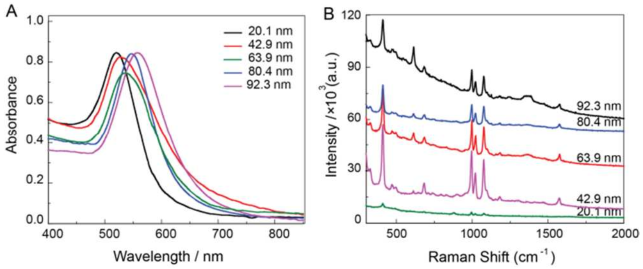

Fig. 2 (A) UV-Vis spectra of unaggregated colloids of different diameter NPs, (B) SERS spectra of different Au colloids recorded 5 min later, after addition of 1 mM thioanisole.

to their small size; however, peak intensities were increased with the passage of time as the mild aggregation proceeds. The TEM images taken after a long time (~ 2 days) indicated that the NPs were only partially aggregated as shown in Fig. 3C-a$_2$. While comparing these results with *ca.* 42.9 nm AuNPs, a slightly obvious broad band representing aggregation was clear in the UV-Vis spectra followed by major decrease in intensity (Fig. 3A-b) whereas SERS spectra showed the highest enhancement signal for *ca.* 42.9 nm which later on continue to decrease until a steady state was achieved (Fig. 3B-b). It is well-known that as the AuNPs size increases, their tendency to form aggregates also increases. The corresponding TEM micrographs (Fig. 3C-b$_2$) showed that this decrease in the intensities in both UV-Vis and SERS spectra was mainly related to the promoted aggregation of the NPs. The addition of thioanisole to the AuNPs solution results in aggregation which generates several "hot-spots" in the nanogaps between neighboring NPs, thus ensuing significant enhancements of the SERS signals.[8] For an optimal SERS performance, the interparticle distance between nanostructures must be in the range of 1-3 nm,[9] and the size should be in the range of 10-100 nm.[10] Decreasing the distance below 1 nm will result in significant decays of SERS performance, due to uncontrolled piling of NPs.[11] Therefore, formation of aggregates after addition of thioanisole resulted in different SERS enhancements depending upon the AuNPs size.

Interestingly, thioanisole showed size-selective fragmentation behavior for the AuNPs. The addition of same concentration of thioanisole in AuNPs solution of *ca.* 63.9 nm resulted in partial fragmentation of the NPs (Fig. 3C-c$_2$). Their UV-Vis (Fig. 3A-c) and SERS spectra (Fig. 3B-c) showed a quite large decrease in intensities that might be initially due to rapid aggregation or later on due to particle size-evolution. To confirm this, HR-TEM micrographs were taken after 70 h which indicated the partial fragmentation of the aggregated AuNPs. From Fig. 3C-c$_2$, it is clearly seen that small particles are shed off from the aggregated Au colloids, so the decrease in intensities in both UV-Vis and SERS spectra could be attributed to the aggregation and partial fragmentation of the Au colloids. Increasing the AuNPs diameter further to *ca.* 80.4 nm and 92.3 nm, we observed the massive aggregation followed by speedy fragmentation as indicated from the visual appearance of the AuNPs solutions and rapid decrease in intensities of the UV-Vis (Fig. 3A-d and 3A-e) and SERS (Fig. 3B-d and 3B-e) spectra. Moreover, their HR-TEM images also showed clearly the fragmented particles (Fig. 3C-d$_2$ and 3C-e$_2$). The initial decrease in SERS enhancements for larger diameter particles might be due to the formation of 'fully-aggregated' plateau that may continue to originate for some time before the fragmentation starts, thus producing less number of 'hot-spots' which gives moderate SERS enhancements.[12]

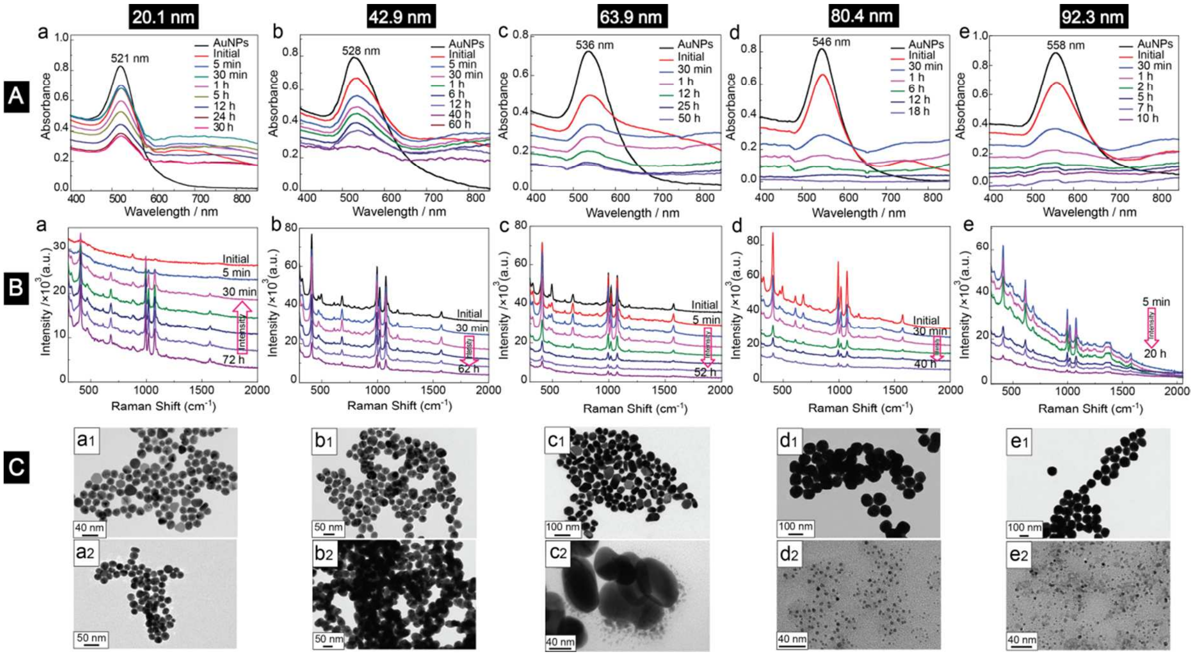

Fig. 3 (A) UV-Vis spectra of AuNPs after addition of 1 mM thioanisole in colloids of (a) 20.1 nm, (b) 42.9 nm, (c) 63.9 nm, (d) 80.4 nm, (e) 92.3 nm, (B) SERS spectra after addition of 1 mM thioanisole in colloids of (a) 20.1 nm, (b) 42.9 nm, (c) 63.9 nm, (d) 80.4 nm, (e) 92.3 nm, (C) TEM micrographs for as synthesized Au colloids and aggregation and fragmentation after addition of 1 mM thioanisole in their aqueous solutions, (a$_1$) original AuNPs, 20.1 nm, (a$_2$) partial aggregation after addition of thioanisole, (b$_1$) original AuNPs, 42.9 nm, (b$_2$) aggregation after addition of thioanisole, (c$_1$) original AuNPs, 63.9 nm, (c$_2$) partial fragmentation after addition of thioanisole, (d$_1$) original AuNPs, 80.4 nm, (d$_2$) fragmentation after addition of thioanisole, (e$_1$) original AuNPs, 92.3 nm, (e$_2$) fragmentation after addition of thioanisole.

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Additionally, the later decrease in intensities might be due to extremely small AuNPs size as confirmed by HR-TEM images (Fig. 3C-d_2 and 3C-e_2), producing no observable SERS enhancements.

According to the experimental results, we assume that more electron injection might be possible for larger NPs as a consequence of more surface loadings which could cross the specific energy threshold so they are fragmented easily than the smaller ones. The quantification of the ligand density onto the surface of AuNPs is beyond the scope of this study, thus we are neglecting here the lateral interactions of the neighboring adsorbed ligands, if any. There are some factors needed to be explained while discussing about the fragmentation phenomenon e.g., surface-to-volume ratio, surface curvature, nanoparticles shape and occupied surface area per particle which corresponds to surface coverage. The large surface-to-volume ratio possessed by small AuNPs makes them more stable[13] to compensate the charge disturbance and less susceptible to fragmentation. Therefore, we deduce such size-dependent fragmentation much related to the surface curvature, surface coverage and surface charges which involves three stages. First is the interaction of thioanisole with AuNPs; second stage involves the aggregation of NPs driven by the replacement of charged ligands by hydrophobic thiol compound; whereas third is the fragmentation of NPs by electron-injection from S to Au surface atoms which makes them highly charged and unstable, therefore releasing this stress by undergoing size-reduction.[3,4] More is the electron-injection to the AuNPs, easier would be the fragmentation which must be related to the surface coverage. Here, the particles shape and size played a prominent role in surface loading of the thiols.[14] According to Cederquist *et al*, increased curvature of small NPs will also result in less surface coverage[15] thus facilitating only a small adsorption of thioanisole. In addition, larger repulsions of electrons due to higher charge density make the electron injection difficult and thus the fragmentation, in turn.[16] Similarly, small surface curvature and large surface area of bigger NPs result in more surface loading of the thioanisole on AuNPs[17] and hence more electron-injection, leading to their fragmentation. Additionally, the shape of larger NPs which is not truly spherical might affect the surface coverage. The larger NPs are considered to be more faceted and crystalline resulting in the greater occupation of the adsorbed ligand at the NPs edges exposed (Fig. S1).[18] Therefore, increased NPs size with more surface coverage resulted in easier fragmentation.

In addition, some intermediate stages of the fragmentation of *ca.* 92.3 nm diameter particles could be clearly observed from Fig. S2, captured by the TEM after 3 h of addition of thioanisole in the AuNPs solution which indicated that there might be several generations of particles with different diameters before the last stable stage is achieved as the fragmentation proceeds with the large NPs (the mean diameters and standard deviation values are given in Fig. S2). The question is that why the AuNPs of diameter *ca.* 20.1 nm or 42.9 nm are not fragmented whereas, the intermediate particles bearing almost the same diameter are fragmented. It could be explained on the basis of the fact that although the particles sizes are same but their surface charges are differently distributed. Once a small particle is dispatched from the surface of large NPs, there must be redistribution of the surface charges on both the parent and newly born NPs. The energy provided by the electron injection to the large NPs may convert to the internal modes of the NPs, depending upon their size.[19] The first generation of fragmentation might gain sufficient energy to propagate or continue the process until a stable size is achieved. To further confirm this assumption, we performed a control experiment to quench the fragmentation process at intermediate stage. 1-hexanethiol was added into the thioanisole containing AuNPs solution of *ca*. 92.3 nm after 4 h. The disappearance of SERS signals (Fig. S3) indicated the detachment of the thioanisole from the surface of the AuNPs and the TEM image in Fig. S4A presented some intermediate sizes for AuNPs. However, the TEM image of the small NPs after 28 h indicated that early generations of fragmentation might continue to fragment although thioanisole is no more attached to the surface (Fig. S4B). As a control, only 1-hexanethiol was added in the AuNPs solution and no such fragmentation was observed after 24 h as shown in Fig. S4C, indicating that AuNPs are not prone to fragmentation by the aliphatic 1-hexanethiol.

In conclusion, we observed that AuNPs within the size domain of 20-100 nm showed selective fragmentation by thioanisole. The changes in the AuNPs morphology were played by their surface charges and surface coverage. As the AuNPs size was increased, it was more likely for them to become small fragments due to less surface curvature and more facets, therefore, they acquired a substantially greater number of thioanisole adsorbed per particle, resulting in more electron injection and easier fragmentation.

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Notes and references

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