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Interaction of ozone with gold nanoparticles

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Abstract

Gold nanoparticles interact with aqueous ozone to produce a surface plasmon resonance shift without aggregation of the nanoparticles. Given ozone's destructive nature, the surprising finding was that the gold nanoparticles returned to their original color and were able to cycle between the wavelengths as ozone was introduced and removed. Gold islands were made and tested for a gaseous ozone response. Similarly to the aqueous system, the gold islands show a cycling effect. Potentially, this system would be useful as a sensor that identifies the presence of ozone in gaseous media.

Keywords: Nanoparticles; Ozone; Surface plasmon resonance

1. Introduction

It has been well documented that bare and substituted gold and silver nanoparticles produce a shift in the absorbance or surface plasmon resonance when an analyte comes into contact with the particle. It is suggested that the shift has been created by aggregation of multiple nanoparticles. Several have suggested the utility of nanoparticle coatings placed on potential sensor platforms [1,2]. We have investigated the interaction of bare gold nanoparticles with ozone.

Our objective is to develop an ozone sensor for the drinking water industry. There is a need for gas and liquid phase ozone sensors. Unfortunately, this task has been complicated by the complex nature of ozone decomposition pathways [3]. For all analytical reagent/ozone reactions, the ozone irreversibly oxidizes the reagent, thus destroying the sensing element [4]. Electrochemically based measurements are problematic due to poor sensitivity and electrode fouling [4]. The prior reports on gold crystals and monolayer surfaces indicated that the ozone decomposed on the surface, but that the surface was unaffected by the ozone [5–7]. Koela exposed Au(1 1 1) at 300 K to ozone. Surface spectroscopy indicated that oxygen covered the surface and that an electron transfer from the Au substrate into the oxygen adlayer occurred [5]. The oxygen could be removed by heating the surface to 600 K; this desorption exhibits first-order kinetics. The Au–O bond dissociation energy is about 58 kcal/mol. Other papers confirmed the need for high temperature and that the ozone decomposes on the metallic surface [6–9].

It seems obvious that ozone would interact with gold nanoparticles (∼25 nm). In addition, we viewed that the shift in the surface plasmon resonance spectrum of gold nanoparticles that adsorbed ozone was a viable approach to circumvent irreversible oxidation issues and make reversible ozone sensors. We anticipated that two problems existed; disaggregating the nanoparticles after the ozone was decomposed and using low temperature to create a reversible surface. This paper reports the results from these experiments.

2. Experimental

Synthesis of gold nanoparticles follows procedures outlined by Hupp and co-workers [1]. To a 500 mL flask, 300 mL of double-distilled deionized (DDDI) water and approximately 0.1 g hydrogen tetrachloroaurate are added. The solution is refluxed with moderate magnetic stirring for 1 h. In

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a separate 50 mL beaker, 0.3 g of sodium citrate is added to 20 mL DDDI and sonicated for 1 min. The entire citrate solution is loaded into a syringe and rapidly injected into the solution's vortex. A color change from pale yellow to deep burgundy is seen in approximately 5 s. The solution is refluxed for an additional 20 min and allowed to cool to room temperature. This stock solution is stored in glass containers in the refrigerator until needed. Particle sizes were determined using a Precision Detector PD 2000 DLS-plus particle sizer.

Ozone generation is performed using a water-cooled Ozone Research Equipment Corporation Model O3B9-0 generator. The cooling water and fan are turned on first. Oxygen pressure from the oxygen cylinder is reduced down to 6 psi by a regulator. The generator is turned on and the electric current set to 1.3 A. This setting should produce approximately 9 g/h of ozone.

Ozone is introduced to the stock gold nanoparticles as follows. The gold nanoparticle solution is diluted down with DDDI until it has an absorbance in the range 0.6–1.0 absorbance units (AU) using a Hewlett Packard 8453 UV–visible Spectrophotometer. Since there is no recorded molar extinction coefficient for gold nanoparticles, an exact concentration cannot be determined. A volume (40 mL) of the diluted gold nanoparticle solution is placed into a 125 mL Erlenmyer flask. The solution is exposed to ozone using a hose tipped with a plastic pipette tip for a preset amount of time (5–45 s). UV–vis spectrum and particle size measurements are then taken. The UV–vis spectrum has a peak at 254 that corresponds to the ozone present in the solutions; peaks ranging from 519 to 540 correspond to the gold nanoparticles. For reversibility studies, the UV–vis spectra were recorded versus time. The loss of the 254 peak indicates all the ozone has decayed or diffused out of solution. The gold particle solution color shifts from deep red (no ozone present) to a bluish-purple (ozone present). Particle sizing is used to determine size of the nanoparticles after reaction with ozone.

The gold islands were made using glass and indium–tin oxide (ITO) coated slides. Glass slides were cleaned using piranha solution and ITO slides were cleaned using a solution of ethanolamine. The slides were coated with chromium and gold using vapor deposition. Both ITO and glass slides were directly coated with gold alone and also with a chromium layer below the gold. After the thin films were prepared they were placed in a vacuum oven at 473 K under 27″ Hg vacuum for 10 min, then allowed to cool in a desiccator. The UV–visible spectra were obtained before and after ozone exposure.

3. Results and discussion

Using a typical solution of bare gold nanoparticles, the baseline particle size was established to be in a range between 20 and 30 nm in diameter. An exact concentration of particles is not known since the molar absorptivity of gold nanoparticles has not been established. Consistent solutions can be made, however, by matching the absorbance of the solutions. Ozone is bubbled into the gold nanoparticle solution and a visible shift in the surface plasmon resonance spectrum is observed. As shown in Fig. 1, the spectrum shifts

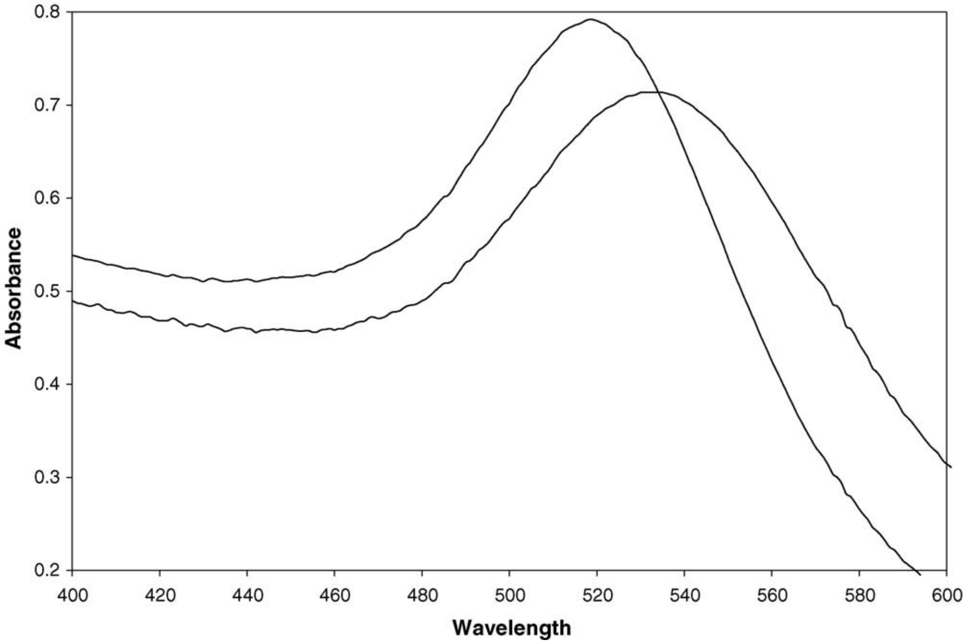

Fig. 1. UV–vis spectra of the gold nanoparticles before interaction with ozone and after interaction with ozone.

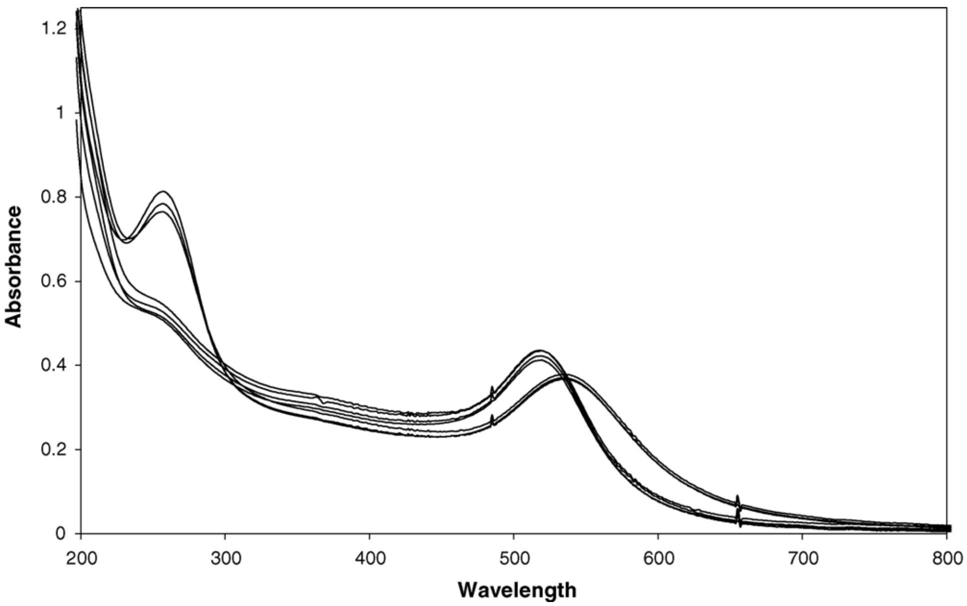

Fig. 2. UV–vis spectra showing the reversibility of the gold nanoparticles.

from about 519 to 540 nm, or from red to bluish-purple. The shift occurs instantaneously upon the addition of ozone gas to the solution. Several other gases were tested such as oxygen, nitrogen, natural gas, and compressed air, but none produced any spectral shift.

When the ozonated gold nanoparticle solution was allowed to stand uncovered at room temperature for 2 h, the surface plasmon resonance spectrum shifted back to the 519 nm peak and the red color. This observation was surprising on two counts. First, from previous studies, the ozone decomposed to oxygen on the gold surface. The removal of oxygen from gold surfaces required high temperatures. After 2 h, however, the gold nanoparticles in a solution containing ozone easily released the chemical species that caused the surface plasmon shift. If it is assumed that the ozone decomposes to oxygen on the surface, then either the small particle size lowers the amount of energy needed to remove oxygen from the gold nanoparticle surface or oxygen is not the species on the particle surface. If ozone is stabilized by the gold nanoparticle, then the amount of ozone on the particle surface would be controlled by an equilibrium between the ozone in solution and the ozone on the particle.

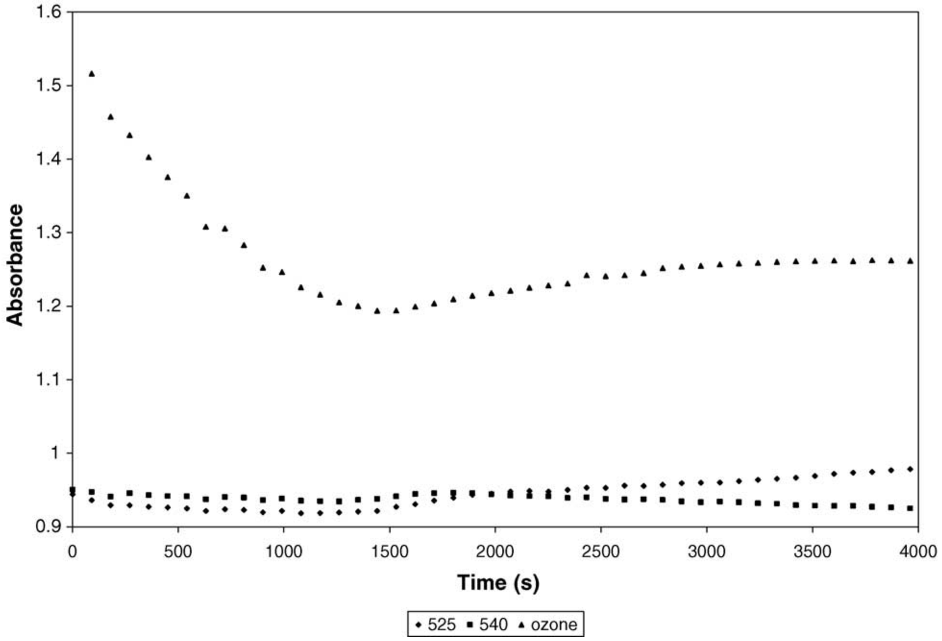

Fig. 3. UV–vis spectra showing the loss of ozone upper trace (triangles), the blue color (squares), and the red color (asterisks).

The second surprise was that even though the color changed, the nanoparticle size did not. In our previous nanoparticle studies, particle sizing experiments clearly showed that bare gold nanoparticles and surface-modified gold nanoparticles exhibited a size population from ∼25–30 nm that increased to ∼50–70 nm after exposure to metal ions. Others have used this information as one piece of evidence for the aggregation hypothesis [1]. In the case of the interaction of gaseous ozone with gold nanoparticles in solution, particle size experiments showed that the size population remained around ∼20–30 nm before and after the observed surface plasmon resonance shift.

A study of this reversibility was performed. Fig. 2 shows that in three straight cycles the surface plasmon resonance peaks returned to 519 nm and shifted to 540 nm in the presence of ozone. The only difference that was observed was a slight (3% total) lowering of the absorbance in the red peak absorbance. The total cycle time was dependent on ozone concentration, but was around 2 min.

Given that the speed of the surface plasmon resonance shift to blue was instantaneous, it was not clear why the reverse shift to red took so long (0.5–2 h). A gold nanoparticle solution was exposed to ozone and the normal shift occurred. Three wavelengths were followed: 254 as an indication of the presence of ozone, 519 as a marker for red gold nanoparticle solution, and 540 as a marker of the blue gold nanoparticles. Fig. 3 shows typical results of this experiment. The upper line is the 254 nm ozone trace. Both the red and blue gold nanoparticle solutions have a significant absorbance at 254 nm that drops quickly. This is attributed to ozone loss through decomposition or diffusion, yet the peak does not fall to zero absorbance. The small rise is due to the increase in the red nanoparticles that have a higher absorbance at 254 nm than the blue. The second line from the bottom is the trace for the blue nanoparticle solution and the bottom trace is for the red nanoparticle solution. A blue color persists until the aqueous ozone is gone (about 1450 s the minimum of the upper trace), then the blue shifts back to red in approximately 550 s (about 2000 s the complete crossover of the blue and red color). The reason that the blue color persists is the large spectral overlap between the red and blues peaks at 540 nm.

Experiments were conducted for different times of ozone exposure to see if the rate of reversibility could be determined. For example, at 5, 10, and 60 s exposures to ozone, the concentration of aqueous ozone was determined to be 2.6, 4.7, and 5.8 mg/L, respectively. All three solutions were blue, but the time it took to lose the ozone and shift back to red was similar at 75 ± 3 min. This suggests that the rate of both ozone decomposition and diffusion from the solution at these concentrations are about the same. This also indicates that gold nanoparticles are sensitive to ozone.

Given that ozone decomposes rapidly as the acid concentration decreases, a pH study was performed using pH values of 2.5, 3.55, 4.53, and 5.51. Unfortunately at pH 2.5 the gold nanoparticles immediately dropped out of solution. At the other three pH values, the time it took for the surface plasmon resonance spectrum to shift was 90, 73.5, and 34.5 min, respectively. This indicates that the rate of reversibility was more dependent on aqueous ozone decomposition than diffusion.

In an attempt to estimate the detection limit of the nanoparticles solution for ozone, shorter exposure times were used. It appears that after 10 s the solutions have reach about 85% saturation. At 1 s exposure, the ozone concentration was 1 mg/L. The surface plasmon shift was complete, indicating that this system has a detection limit below the 1 mg/L level. This system does not appear to be useful for quantitation, but could be used as an indicator of the presence of ozone for indoor environments or personnel safety devices.

Other gases like nitrogen, carbon monoxide, and nitrous oxides were tested. Only nitrous oxide exhibited an effect that was a complete and instantaneous precipitation of the particles in solution. It was suggested that the citrate present was involved. Gold nanoparticles made by other synthetic paths without citric acid produced the same results. In addition the gold nanoislands described next had no citrate ions presence but exhibited the same color shift response to ozone. This

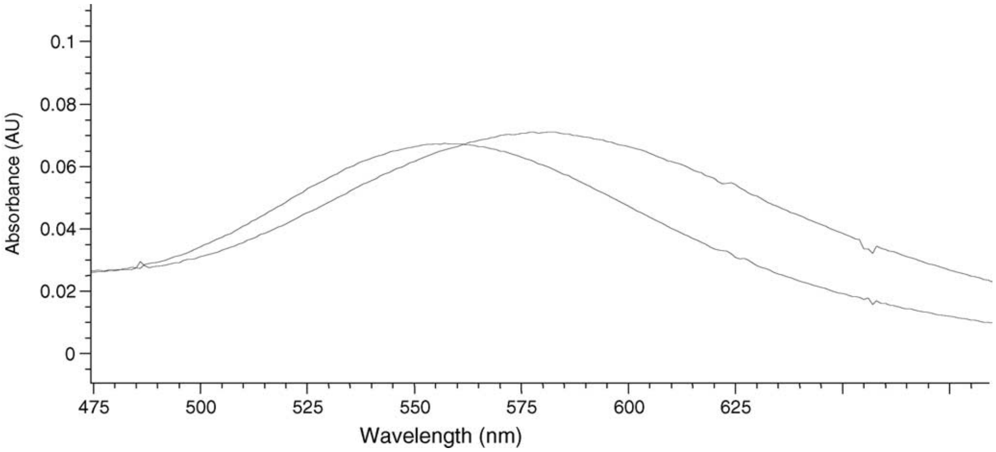

Fig. 4. UV–vis spectra showing the gold island ITO slide before and after exposure to gaseous ozone.

would suggest that citrate ion is not essential to the observed phenomenon.

Since nanoparticles in solution had sensitivity to ozone, nanoparticles out of solution were also investigated. Combination slides were prepared with a first layer of about 19 Å of chromium and second layer of about 24 Å of gold. The gold only slides had about 24 Å of gold. Reference reports indicate that with the vacuum oven heating, the gold anneals into gold islands [10]. These islands can behave as gold nanoparticles but without the aggregation requirement. Gaseous ozone was passed over the slides for 1 h and a shift from pink to blue was observed.

Fig. 4 shows how the surface plasmon resonance spectrum shifts on the ITO glass slide. The surface plasmon resonance spectrum changed from 549 to 565 nm for the glass slides coated by chromium and gold, and 558–583 nm for the ITO slide coated with only gold. The glass slide with gold only did not yield reproducible results. At room temperature the slides will return to ∼552 nm after a day. The slides can cycle similarly to the gold nanoparticle solutions.

4. Conclusion

The data presented gives a general insight into ozone influences over gold nanoparticles, both in solution and out. Although the cycling aspect is relatively slow at room temperature, other conditions may prove more favorable in rapid return to baseline. Despite the lengthy cycle time, any return without intense heating is appreciable. Further work with both the nanoparticle solutions and nanoparticles on glass surfaces may prove promising for constructing reusable ozone sensors that operate at room temperature.

Acknowledgement

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