ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 69 (2006) 873–876

Talanta

www.elsevier.com/locate/talanta

Solution ionic strength effect on gold nanoparticle solution color transition

C. Burns, W.U. Spendel, S. Puckett, G.E. Pacey [*]

Miami University Center for Nanotechnology, Department of Chemistry and Biochemistry, Miami University, Oxford, OH 45056, USA

Received 13 July 2005; received in revised form 11 November 2005; accepted 13 November 2005

Abstract

Unmodified and modified gold nanoparticles are proposed as sensors using the red to blue transition as an indicator. This work indicates that ionic content is an important variable to track in analytical samples and during the sensor fabrication processes. Mono and multivalent salts where the titrants for a standard gold nanoparticle solution. Multivalent cation salt titrants exhibited a greater sensitivity to color change than monovalent cation salts. The data suggest that specific surface adsorption is the predominant mechanism for the red to blue color change not aggregation. The 3–7 nm Debye length for divalent cations versus the 0.5–1.5 nm for monovalent cations indicates surface electrodynamic resonance effects are an important factor in the observed color changes.

Keywords: Gold nanoparticles; Ionic strength; Surface plasmons

---

1. Introduction

There have been numerous reports of the use of both bare and surface modified gold nanoparticles as a spectrophotometric reagent [1–4]. Both bare and surface modified gold nanoparticles exhibit a red to blue color change in the presence of certain interactive analytes. Gold nanparticles with particle sizes between 15 up to 150 nm exhibit a red color due to surface plasmon resonance. The effect is due to particle size and Mie light scattering [5]. Since nanoparticle size, surface modification, medium dielectric constant, particle long distance proximity, and particle size all affect gold nanoparticle light scattering, a color transition can result from multiple mechanisms. The proposed mechanism for the red to blue shift is that the gold nanoparticles aggregate into larger nanoparticles. However, we recently discovered an exception to this rule when it was observed that a 25 nm bare gold nanoparticle would reversibly cycle between the red and blue colors in the presence of ozone without aggregation [6].

During the routine investigation of surface modified gold nanoparticles, it was observed that the ionic strength of the solution may also play a role in the color transition. It is known that surface charge, due to adsorbed species on the gold nanoparticle surface will affect the nanoparticle solution stability and Brownian motion interparticle closest approach mean distance. Since ionic strength determines the Debye length [7] around the particle we hypothesized that ion strength will change the mean closest approach distance between the gold particles. Consequently, by using ionic strength, it is possible to adjust the mean encounter distance between gold nanoparticles and the subsequent effect on the observed color change. This paper provides the data that demonstrates the ionic strength effect on gold nanoparticles.

2. Experimental

2.1. Chemicals

The following salts were used in this experiment: ammonium nitrate, ammonium sulfate, ammonium phosphate, cesium nitrate, cesium sulfate, chromium potassium sulfate, cupric sulfate, iron(II) sulfate, iron(III) sulfate, lead nitrate, lithium nitrate, magnesium nitrate, magnesium sulfate, potassium chloride, potassium nitrate, potassium sulfate, potassium phosphate, rubidium chloride, rubidium nitrate, rubidium sulfate, ruthenium(III) chloride hydrate, sodium chloride, sodium nitrate, sodium sulfate, sodium phosphate, zinc nitrate were purchased from Aldrich Chemical Co. (Milwaukee, WI).

Synthesis of gold nanoparticles follows procedures outlined by Hupp and co-workers [8]. To a 500 mL flask, 300 mL of

---

[*] Corresponding author.
E-mail address: paceyge@muohio.edu (G.E. Pacey).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.11.038

Table 1
Salts used and their physical properties

Salt	Cation charge	Anion charge	Concentration (M)	Ionic strength	Activity coefficient	Debye length (nm)
Ammmonium sulfate	1	2	0.1	0.3	0.44	1.4
Ammonium nitrate	1	1	0.1	0.1	0.76	1
Calcium chloride	2	1	0.1	0.3	0.44	3.6
Calcium nitrate	2	1	0.1	0.3	0.44	3.6
Cesium nitrate	1	1	0.1	0.1	0.76	1.5
Cesium sulfate	1	2	0.001	0.003	0.89	2.6
Iron(II) sulfate	2	2	0.001	0.004	0.76	6.1
Iron(III) sulfate	3	2	0.001	0.015	0.47	4.6
Lead nitrate	1	1	0.001	0.001	0.97	9.5
Lithium nitrate	1	1	0.1	0.1	0.76	1.2
Magnesium chloride	2	1	0.001	0.003	0.89	7.9
Magnesium nitrate	2	1	0.1	0.3	0.44	7.8
Magnesium nitrate	2	1	0.001	0.003	0.89	7.8
Magnesium sulfate	2	2	0.001	0.004	0.76	6.5
Potassium nitrate	1	1	0.1	0.1	0.76	1.4
Potassium phosphate	1	3	0.1	0.6	0.22	0.6
Rubidium nitrate	1	1	0.1	0.1	0.76	1.3
Rubidium sulfate	1	2	0.1	0.3	0.44	0.8
Ruthenium chloride	3	1	0.001	0.006	0.78	8.4
Sodium chloride	1	1	0.1	0.1	0.76	1.2
Sodium nitrate	1	1	0.1	0.1	0.76	1.2
Sodium phosphate	1	3	0.1	0.6	0.22	0.5
Zinc nitrate	2	1	0.001	0.003	0.89	6.9

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 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 pastic containers in the refrigerator until needed. The 15% gold nanoparticle solutions were obtained by adding 15 mL gold nanoparticle solution to 85 mL distilled water.

2.2. Apparatus

Titration experiments were performed with a conventional 50 mL burette. Different solutions of salts were used as titrants, and each titrant solution was added to the gold analyte solution until the gold color change was observed. In this experiment, the titration end-point was a color change of red to purple. Solutions were titrated to a point just short of the endpoint and then absorbance of the solution was measured using a HP 8453 A UV–vis diode array spectrophotometer. In addition, the sizes of the particles were measured using a precision detector PD 2000 DLS-plus particle sizer. The solutions were then titrated beyond the endpoint and reanalyzed by both the UV–vis and particle sizer.

3. Results and discussion

Gold nanoparticles, modified and unmodified, change color from red to blue upon interaction with various species. Two proposed mechanisms for the color change are: gold particles physically coalescing to form larger particles, or mean interaction distances reducing such that their surface plasmons interact. Experience in our laboratory using gold nanoparticles to form sensors show they change color readily when exposed to a wide variety of analytes. This study was undertaken initially to probe the mechanism for the gold nanoparticle color change, and to determine design rules for making gold nanoparticle-based sensors. Table 1 displays the salts tested, the maximum concentration of salt used for the standard gold solution, ionic strength, calculated activity coefficient (using extended Debye–Huckel), and calculated Debye length for unmodified gold nanoparticles.

A representative spectral shift example for monovalent and divalent cationic salts is shown in Figs. 1 and 2. Untreated gold nanoparticles have an absorbance peak at 520 nm. Fig. 1 shows the volume normalized gold nanoparticle spectra just before the gold red to blue transition. Introducing the salt causes a slight red shift in the gold peak maximum of 519, 524 nm for sodium

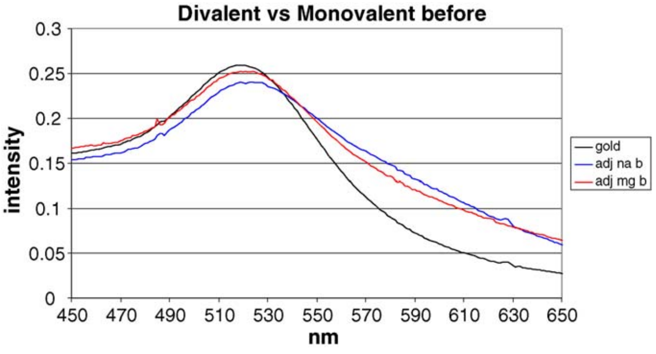

Fig. 1. Gold nanoparticle spectra just before the endpoint.

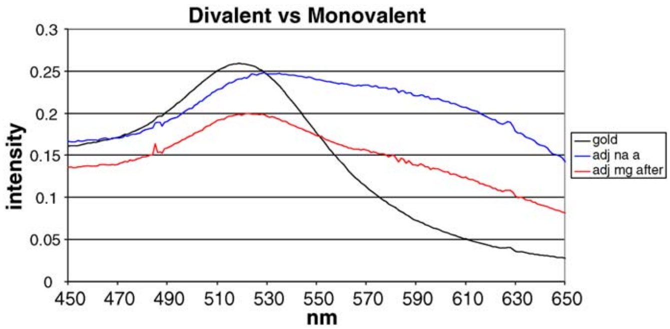

Fig. 2. Gold nanoparticle spectra after endpoint.

and 521 nm for magnesium salt. Following the maximum peak evidence of the endpoint is seen in the broadening of all three of the spectrums. Further addition of a small amount of salt results in the red to blue color change and significant broadening of the spectrum to the red. Fig. 2 shows the spectrum shift right after the color changes. The monovalent sodium salt broadens the spectrum to a greater extent than the divalent magnesium salt.

In these experiments, a known concentration of standard gold nanoparticle solution was titrated by an inorganic salt. The titration was carried out to the endpoint with a goal of using a volume of gold nanoparticle solution between 20 and 45 mL. The first obvious point is that monovalent salts could be as concentrated as 0.1 M and still meet the titration goal. However, multivalent cation salts exhibited a maximum concentration of 0.001 M. Since the titration was not based on a stoichiometric relationship like neutralization or oxidation–reduction, but on the amount of salt needed to produce a change of the surface properties of the gold nanoparticle, multivalent anion salts acted like monovalent cation salts.

The data in Table 2 clearly shows that the titration does not force the gold nanoparticle to aggregate. The nanoparticle size after the titration is either within the experimental error the same or smaller. These results suggest that the repulsion distance between the charged gold nanoparticles has changed and that the salt components must be adsorbing to the surface. This effect does not seem to be size depend in the sub 100 nm range since gold nanoparticles half the size shown in Table 2 exhibited the same behavior.

It is known that salt solution ionic strength is a particle-independent way to alter the repulsion distance between charged particles. Increasing ionic strength decreases the Debye length [9]. As the Debye length decreases, the averaged distance of closest approach between particles decreases. As this distance decreases, we expect the surface plasmon communication between gold particles to become stronger. Assuming the mean interaction distance between gold nanoparticles is a significant contributor to the color change, ionic strength should cause a nanoparticle surface plasmon color change.

Table 2
Particle size data

Salt	Average size (nm) before small particle population	Average size (nm) after small particle population	$n = 3–4$
Cesium nitrate	34	34	±3.5
Ammonium nitrate	35	41	±4.0
Rubidium nitrate	37	39	±3.8
Magnesium nitrate	39	38	±3.8
Sodium nitrate	50	42	±5.0
Potassium nitrate	59	52	±5.8

Table 3
Zeta potential before and after titration

Salt	Gold nanoparticle mobility/zeta potential	
	At titration start	At titration endpoint
Magnesium nitrate	−1.44	0.07
Calcium chloride	−1.16	0.08
Magnesium chloride	−0.94	0.29
Sodium chloride	−0.86	0.04
Sodium nitrate	−0.82	0.1
Calcium nitrate	−0.66	0.08

Table 3 shows the zeta potential values for the nanoparticles before and after the titration. The data clearly shows that the charge on the gold nanoparticle is eliminated by the titration by the salt.

The combined data suggest the following. Since a longer Debye length indicates greater particle–particle distances, on average and despite the strong concentration effect (two orders of magnitude), the gold nanoparticles are further apart for divalent cations than monovalent cations. Consequently, the more pronounced effect on the gold nanoparticle color change is due to cation surface adsorption rather than the ionic strength effect of allowing charged particles to aggregate.

4. Conclusions

Specific cation adsorption from salt solution onto gold nanoparticles will change their color from red to blue. Divalent cations are more effective than monovalent ions. Ion adsorption onto the gold particle affects the gold surface plasmon state as do changes in the dielectric constant around the gold nanoparticle surface. Specifc ion surface adsorption is the predominant mechanism for the red to blue color change. The 3–7 nm Debye length for divalent cations versus the 0.5–1.5 nm for monovalent cations is indicative of the resonant electrodynamic communication distance between gold nanoparticles. Therefore, the ionic strength mediated reduced average interparticle distance is not responsible for the color change. Consistent with the large difference between monovalent and divalent cations, the gold nanoparticle is expected to have a negative surface charge, attracting the cations into the Stern layer. Varying the anion while keeping the sodium cation fixed indicates the anion weakly contributes to the apparent particle surface dielectric constant. In contrast, the magnesium cation overwhelms the anion effect. Due to their negative charges, the anions are further away from the gold surface in the electric double layer, suggesting the surface plasmon is influenced primarily by the adsorbed ions in the Stern layer.

References

[1] N.K. Chaki, T.G. Gopakumar, M. Aslam, K. Vijayamohanan, Encycloped. Nanosci. Nanotechnol. 5 (2004) 861.

[2] M-C. Daniel, D. Astruc, Chem. Rev. (Washington, DC, United States) 104 (1) (2004) 293.

[3] J.L. West, N.J. Halas, Annu. Rev. Biomed. Eng. 5 (2003) 285.

[4] K.G. Thomas, P.V. Kamat, Acc. Chem. Res. 36 (12) (2003) 888.

[5] M. Vollmer, U. Keibig, Material Science, vol. 25, Springer–Verlag, 1995.

[6] S.D. Puckett, J.A. Heuser, J.D. Keith, W.U. Spendel, G.E. Pacey, Talanta 66 (2005) 1242–1246.

[7] J. Israelachvili, Intermolecular and Surface Forces, second ed., Academic Press, 1991, pp. 32, 213–254.

[8] Y. Kim, R.C. Johnson, J.T. Hupp, Nano Lett. 1 (2004) 165.

[9] R.J. Hunter, Foundations of Colloid Science, vol. 1, Clarendon Press, Oxford, 1993, pp. 329–341, 415–418.