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Investigating the Effects of Some Capping Agents upon Gold Nanocrystals Stability, Size and Surface Plasmon Resonance

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Abstract

A colloidal synthesis of gold nanocrystals with different capping agents is reported. 1-Dodecanethiol (1), Dodecylamine (2), *Tri-n*-octylphosphine (3) (*TOP*) and *Tri-n*-octylphosphine oxide (4) (*TOPO*) were used as capping agents and the gold nanocrystals stability, size and surface plasmon resonance (*SPR*) were investigated.

Keywords: Gold nanocrystals; Surface plasmon; Dodecylamine; *Tri-n*-octylphosphine; *Tri-n*-octylphosphine oxide

Introduction

Metal clusters have been used in industry and material chemistry since 18th century. Since nanoscale metals can absorb and scatter visible light, they were being used as coloring agents in glass industry [1,2].

In recent years metal nanocrystals have found extensive applications in different branches of science and technology such as nano optics [3-6], sensors [3-6], nanoelectronics [7], single electron devices [8,9] and metal-semiconductor nanocomposites [10-12].

Gold nanocrystals display many interesting optical [13], electronic [5,14,15] and chemical properties [5,11,12] that are size-dependent.

They can be used in composite systems with semiconductor nanostructures to improve the photo catalytic properties and promote interfacial charge transfer processes in semiconductor nanoparticles [11,12].

Self-assembling nature of a gold colloidal particle monolayer can be used in single electron and semiconductor devices [7,14,15].

Also gold nanoparticles have found increasing applications in biology and medicine [16].

The common method of colloidal metal nanocrystals synthesizing is, metal salt reduction with different reducing agents such as sodium borohydride, citrate, phosphorous or ascorbic acid [2].

To prevent nanoparticles from irreversible aggregation and in order to prepare a monodisperse colloid, surface passivants or capping agents are used. Capping agents are mostly, organic compounds which can provide steric hindrance, like long chain alkyl thiols [17,18], alkyl amines like 1-pentadecylamine [19] and octadecylamine [20] and phosphines like triphenyl phosphine [21].

Organic linear molecules which are used as capping agents can act as tunnel junctions between metallic nanoparticles, so there is an interest in preparing gold clusters which are passivated with these molecules due to their potential applications in single electron tunneling [17,22].

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The present report includes colloidal synthesis of gold nanocrystals. 1-Dodecanethiol (1), Dodecylamine (2), *Tri-n*-octylphosphine (3) (*TOP*) and *Tri-n*-octylphosphine oxide (4) (*TOPO*) were used as capping agents. The developed method by *Brust et al.* [18] (who used 1 as capping agent), was chosen for preparing gold nanocrystals and the resulting nanocrystals stability, size and surface plasmon resonance were investigated.

Experimental

All experiments took place in the ambient temperature and pressure.

Deionized (*DI*) water with a conductivity of 17 MΩcm was used in the experiments. A transmission electron microscope (*TEM*) (*Philips EM 208 S*, 100kV accelerating voltage) was used to take images.

UV-Vis spectra were recorded on a *Hitachi U3410* spectrophotometer.

Except compounds 3 and 4, which were purchased from *Alfa Aesar* chemicals, other chemical reagents and solvents were purchased from *Merck* chemicals and used without further purification.

1 mmol tetrachloauric (*III*) acid trihydrate (5) (0.55 g) was dissolved in 45 ml of *DI* water (aqueous phase). 5 mmol tetraoctylammonium bromide (6) (3.00 g) was used as phase transfer reagent and was dissolved in 120 ml of toluene (organic phase). When the aqueous phase was mixed with the organic phase, tetrachloroaurate was transferred into the organic phase according to the color exchange between two phases. In this time two phases were separated and the organic phase was divided into

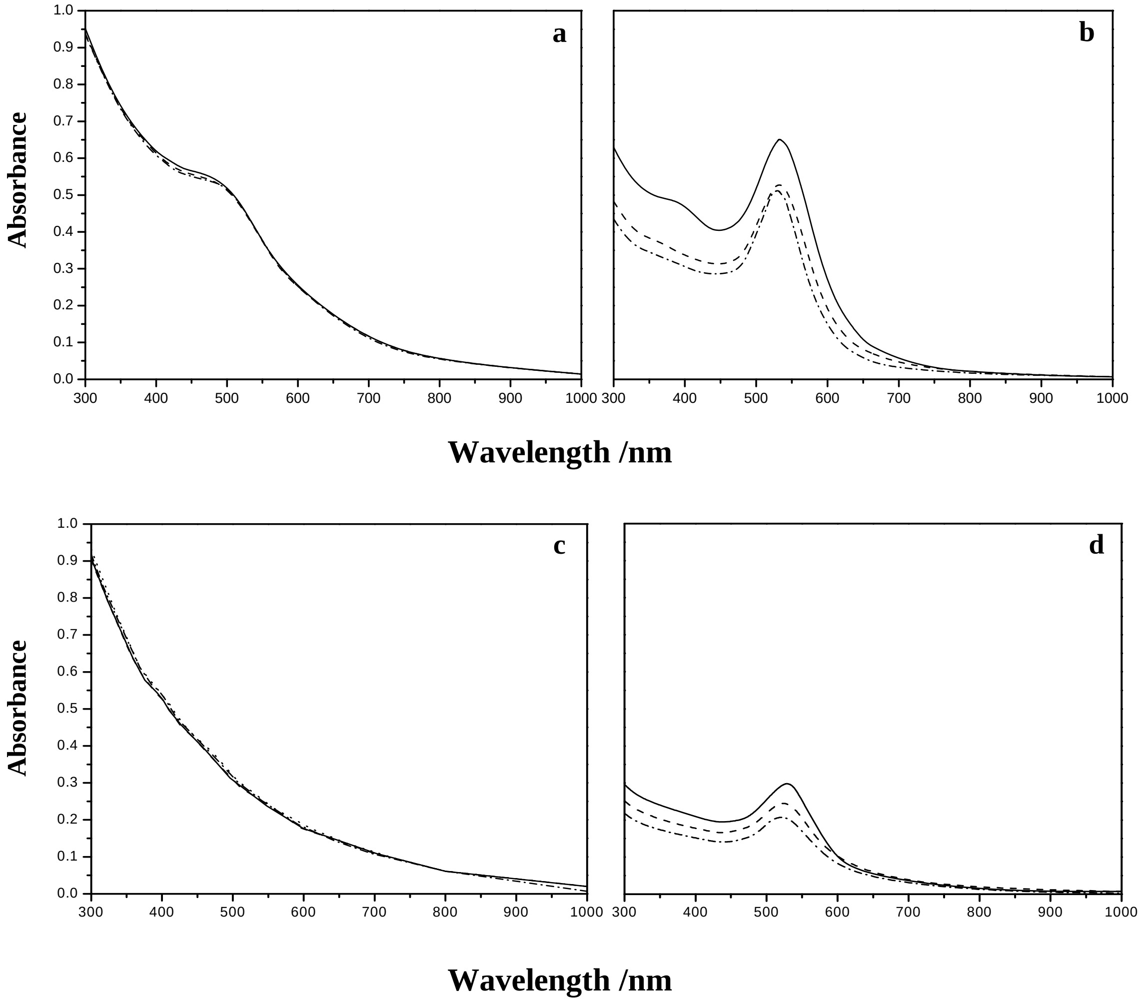

Figure 1. Absorption spectra of a) 1, b) 2, c) 3, d) 4, capped gold nanocrystals which were kept at 3°C. The spectra were recorded during three months. Solid line is the as prepared solution's spectrum, dashed line is the spectrum after one month and dashed-dotted line is the spectrum at the end of the third month.

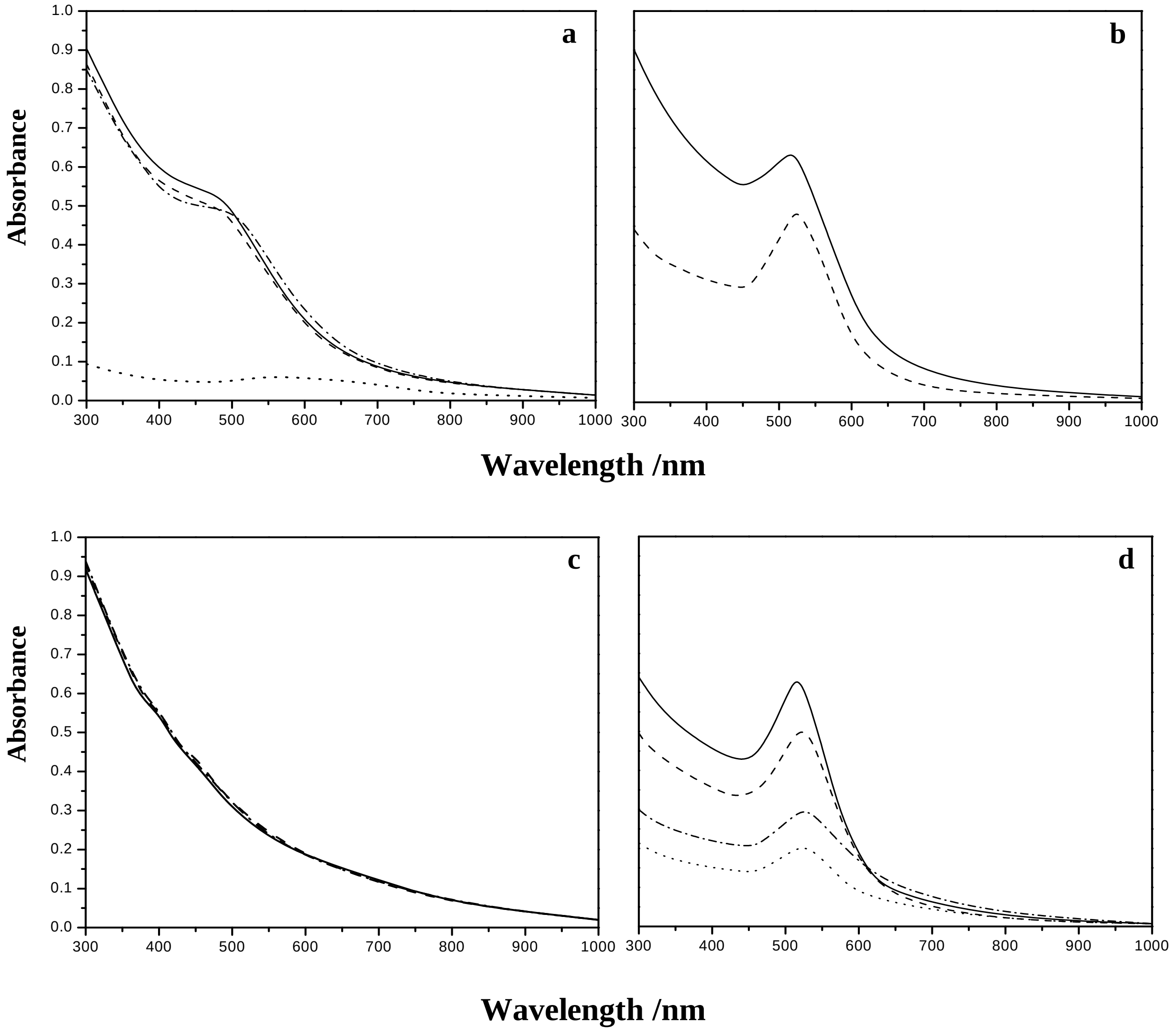

Figure 2. Absorption spectra of a) 1, b) 2, c) 3, d) 4, capped gold nanocrystals which were kept in ambient temperature. The spectra were recorded during one month except (b) which lost its color after two weeks. Solid line is the as prepared solution's spectrum. Dashed, dashed-dotted and dotted lines are the spectra which were recorded after the second, third and fourth weeks, respectively.

four parts. The experiment was continued in parallel. 1 mmol 1 (0.2 ml) was added to the first part, 1 mmol 2 (0.15 g) was added to the second part, 1 mmol 3 (0.4 ml) and 1 mmol 4 (0.3 g) were added to the third and fourth parts, respectively. When 1 and 3 were added to the organic phase the solutions became transparent.

A freshly prepared aqueous solution of sodium borohydride (7) was slowly added with vigorous stirring to each solution. 4 mmol 7 (0.148 g) in 10 ml *DI* water was prepared for each solution. Further addition of reducing agent took about 3 h for each solution. When 7 was added completely, the solutions were stirred for about 2 h. As soon as 7 was added to the solutions the first one's color changed to deep purple. The second solution's color changed to deep red. The third one changed to deep brown and the fourth one changed to yellowish brown.

The organic phases were separated and dried with sodium sulphate. The dried organic phases were evaporated in a rotary evaporator until when about 5 ml of each of them remained. They were mixed with ethanol and were kept for 12 h at −9°C. The dark precipitates were separated and washed with ethanol and dissolved in about 10 ml toluene. Ethanol was added to the toluene solutions and the precipitation step was repeated and precipitates were dissolved in toluene.

Results and Discussion

From the color of solutions we can guess the size of

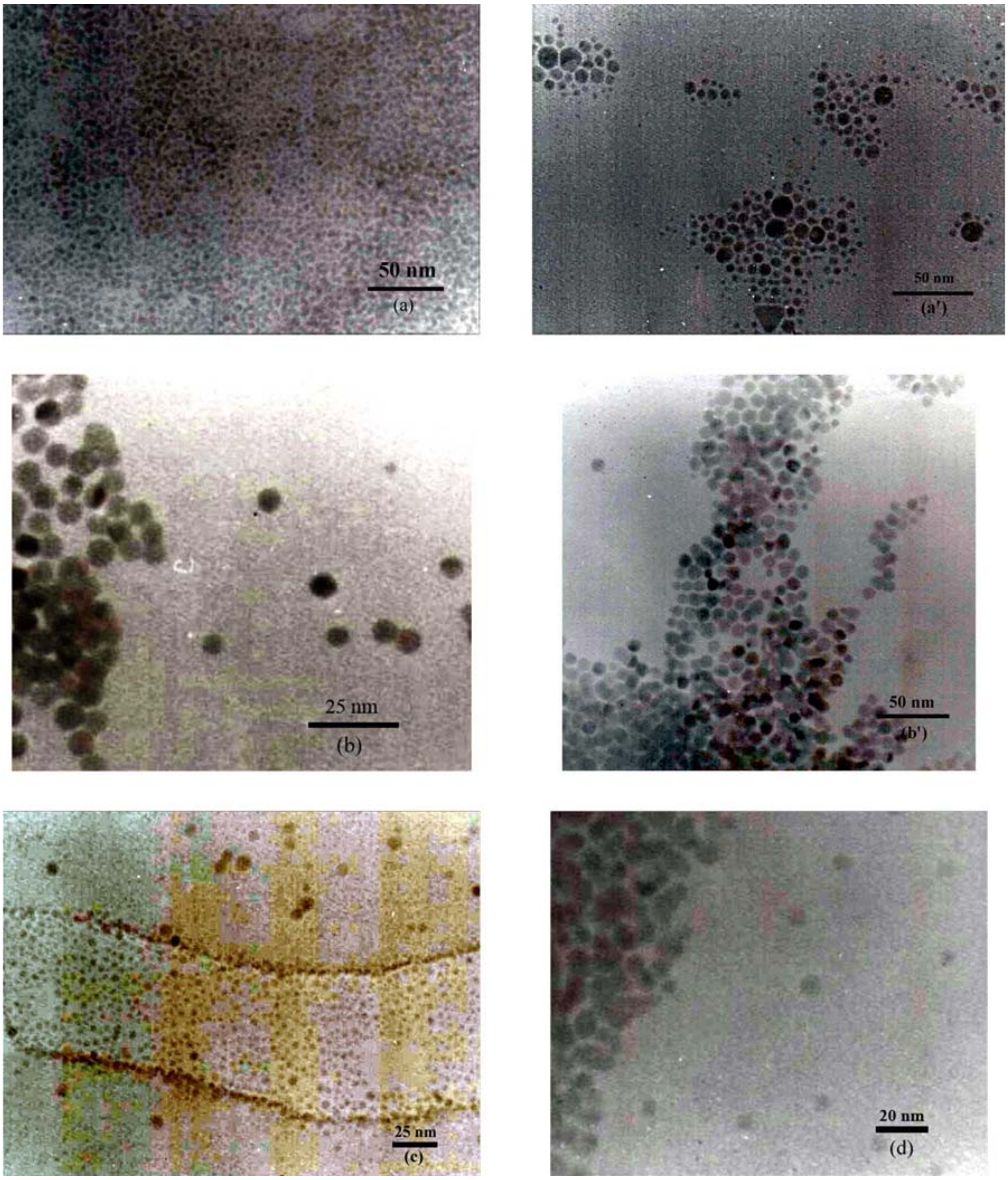

Figure 3. *TEM* images of a) 1, b) 2, c) 3, d) 4, capped gold nanocrystals. a′) and b′) show size distribution in 1 and 2 capped gold nanocrystals.

nanoparticles [2]. Since the toluene colloidal solutions of 4 and 2 capped gold nanocrystals were pink and deep red, respectively, we expected they must have had sizes more then 5 nm. They showed good plasmon resonances (Figs. 1b, 1d, 2b and 2d). In Figures 1 and 2 the solid lines are the absorption spectra of the as prepared solutions. In Figure 1 dashed line is the spectrum after one month and dashed-dotted line is the spectrum at the end of the third month. In Figure 2 dashed, dashed-dotted and dotted lines are the spectra which were recorded after the second, third and fourth weeks, respectively. 1 and 3 capped gold nanocrystals were brown and yellowish brown, respectively; so, we expected that they must have had sizes less than 5 nm (Figs. 3a, 3c). 3 capped gold nanoparticles did not show surface plasmon resonance and they did not have any absorption at around 520 nm (Figs. 1c and 2c). In these particles damping effect of capping agents upon the surface plasmon resonance is significant because the surface to volume ratio in particles size less than 5 nm is considerable. 1 capped gold nanocrystals did not have absorption at around 520 nm, too. They only had a shoulder at higher energies in their absorption spectra, which can be the result of interband transitions [2].

Transmission Electron Microscope (*TEM*) images confirmed our predictions. Representative *TEM* images are given in (Fig. 3). The specimens for electron microscopy were prepared by evaporation of two drops of toluene solutions of nanocrystals on carbon coated copper grids.

Among these four types of gold nanocrystals, 2 capped nanocrystals (Fig. 3b) showed the narrowest size distribution (Fig. 3b′). On the contrary, 1 capped nanocrystals (Fig. 3a) showed the widest size distribution (Fig. 3a′).

The prepared colloidal solutions were kept in ambient temperature and in refrigerator at 3°C. Intensity reduction in absorption spectra in Figures 1 and 2 (which have been showed with dashed, dashed-dotted and dotted lines) during the time shows the stability of colloidal particles which have been capped with different capping agents. The samples which had been kept in refrigerator were very stable over a period of three months. In this condition 2 and 4 capped particles showed just a little damping in their absorption spectra, which by far was less than those kept in ambient temperature (Figs. 1b, 1d and 2b, 2d).

In ambient temperature 2 and 1 capped samples which had been used for absorption spectroscopy lost their colors after about two weeks and one month, respectively (Fig. 2b, 2a).

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References

1. Sandrock M.L., Pibel C.D., Geiger F.M., and Foss C.A. *J. Phys. Chem. B.*, **103**: 2668 (1999).
2. Bauer G., Hassmann J., Walter H., Haglmuller J., Mayer C., and Schalkhammer T. *Nanotechnology.*, **14**: 1289 (2003).
3. Huang S., Minami K., Sakaue H., Shingubara S., and Takahagi T. *J. Appl. Phys.*, **92**(12): 7486 (2002).
4. Kawata S., Ohtsu M., and Irie M. *Nano-Optics*. Springer-Verlag, Berlin, Heidelberg (2002).
5. Kamat P.V. *J. Phys. Chem. B.*, **106**: 7729 (2002).
6. Kim K. and Lee I. *Langmuir*, **20**: 7351 (2004).
7. Vidoni O., Neumeier S., Bardou N., Pelouard J.L., and Schmid G. *J. Cluster. Sci.*, **14**(3): 325 (2003).
8. Shipway A.N., Katz E., and Willner I. *CHEMPHYSCHEM*, **1**: 18 (2000).
9. Bezryadin A., Dekker C., and Schmid G. *Appl. Phys. Lett.*, **71**(9): 1273 (1997).
10. Heath J.R., Knobler C.M., and Leff D.V. *J. Phys. Chem. B.*, **101**: 189 (1997).
11. Subramanian V., Wolf E., and Kamat P.V. *Ibid.*, **105**: 11439 (2001).
12. Dawson A. and Kamat P.V. *Ibid.*, **105**: 960 (2001).
13. Kamat P.V. and Shanghavi B. *Ibid.*, **101**(39): 7675 (1997).
14. Sato T. and Ahmad H. *Appl. Phys. Lett.*, **70**(20): 2759 (1997).
15. Sato T., Ahmad H., Brown D., and Johnson B.F.G. *J. Appl. Phys.*, **82**(2): 696 (1997).
16. Salata O. *J. Nanobiotech.*, **2**: 3 (2004).
17. Gutierrez-Wing C., Ascencio J.A., Perez-Alvarez M., Marin-Almazo M. and Jose-Yacaman M., *J. Cluster. Sci.*, **9**(4): 529 (1998).
18. Brust M., Walker M., Bethell D., Schiffrin D.J., and Whyman R. *J. Chem. Soc. Chem. Commun.*, 801 (1994).
19. Brown L.O. and Hutchison J.E. *J. Am. Chem. Soc.*, **121**: 882 (1999).
20. Chen X.Y., Li J.R., and Jiang L. *Nanotechnology*, **11**: 108 (2000).
21. Yang H.T., Shen C.M., Wang Y.G., Su Y.K., Yang T.Z., and Gao H.J. *Nanotechnology*, **15**: 70 (2004).
22. Ascencio J.A., Mendoza M., Santamaria T., Perez M., Nava I., Gutierrez-Wing C., and Joze-Yacaman M. *J. Cluster. Sci.*, **13**(2): 189 (2002).