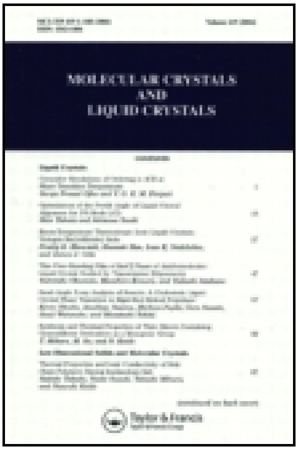

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and pH Dependent Optical Properties of Gold Nanoparticles Capped with Mercaptopropionic Acid

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To cite this article: S. T. Liu, T. Zhu, Y. C. Wang & Z. F. Liu (1999): Synthesis and pH Dependent Optical Properties of Gold Nanoparticles Capped with Mercaptopropionic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 245-248

To link to this article: http://dx.doi.org/10.1080/10587259908023423

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 245-248
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Printed in Malaysia

Synthesis and pH Dependent Optical Properties of Gold Nanoparticles Capped with Mercaptopropionic Acid

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A simple method is reported for preparing gold nanoparticles capped with 3-mercaptopropionic acid(MPA). The capped Au nanoparticles can be isolated as a dark brown solid which can be re-dispersed in sodium hydrate solution. The average size of nanoparticles is 4.9±0.7 nm, determined by HRTEM. The surface plasmon band of Au nanoparticles around 520nm was found red-shifted together with a slight damping and broadening, as the pH of the colloid is adjusted from 11 to 3.5. Such a shift is attributed to the pH dependent surface charge of the nanoparticles.

Keywords: Gold nanoparticles; Mercaptopropionic acid; HRTEM; UV-Visible spectroscopy

INTRODUCTION

Recently, there has been an increasing interest in the synthesis of semiconductor and metal nanoparticles, due to the unique optical, electrical properties as well as the potential applications of such an advanced materials[1]. A large number of preparation methods have been developed, most of them involve the chemical reduction of a relevant metal salt in the presence of suitable surfactants, which serve as stabilizers to prevent aggregation. One of the limitations to thus-prepared colloidal nanoparticles is that, they can not be isolated and re-dispersed in selected solvents after precipitation, leading to the difficulty in further refinement and applications. Brust et al. made an important effort to overcome this limitation, who established a method to prepare thiol-capped gold nanoparticles, in which the formation and growth of gold particles as well as the attachment of thiol molecules occur almost simultaneously. This method has been extended to synthesize gold nanoparticles derivatised with bifunctional thiols[2].

The optical properties of metal nanoparticles are found to be dependent on the size, surface composition, medium, and so on[3-5]. Chemical modification of nanoparticles can provide more freedoms to regulate their optical properties. For example, Whitesides et al. [3] and Sastry et al. [5] have studied the gold and silver nanoparticles capped with thiols terminated with various functional groups by UV-Vis spectroscopy, respectively.

In this paper, we use a single phase technique, in which all the reactants were dissolved in the same solvent, to prepare MPA-capped gold nanoparticles by chemical reduction. The dissociable surface -COOH groups make it possible to regulate the optical properties of gold nanoparticles by simply changing the solution pH. We monitored the surface plasmon peak with the change of solution pH by UV-Visible spectroscopy.

EXPERIMENTAL

Gold colloids were synthesized following a procedure in Ref.[2] with a slight modification. Sixty milligrams of $HAuCl_4{\cdot}3H_2O$ was dissolved in ethanol(150ml), then 3.5mg MPA was added. While the mixture was vigorously stirring, a solution of 50mg $NaBH_4$ in 100 ml ethanol was added drop by drop. After further stirring for a few hours, the mixture containing a dark brown precipitate was filtered. The precipitate was washed with ethanol, and dried in vacuum. Finally, the product was re-dissolved in an alkaline aqueous solution (pH=11), which serves as the stock colloids.

Samples for TEM (Hitachi-9000) observation were prepared by drop-casting. One drop of the stock colloid was put onto a carbon coated copper grid, and dried in air. The acceleration voltage is 300kV.

The pH of the gold colloid was adjusted in the range of 11-3.5 by titration of the stock colloid with 0.01 mol/l aqueous HCl. Absorption spectra were monitored with a JASCO V-500 spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows a HRTEM image of MPA-capped gold nanoparticles. The size distribution was obtained by measuring over 100 particles in an arbitrarily chosen area of a TEM image. The mean size of gold nanoparticles is 4.9±0.7 nm in diameter. Actually, we can obtain different size of nanoparticles by adjusting the molar ratio of the thiol to the gold salt. Atomic Au lattice fringes can be observed in some area of Fig. 1, indicating that the gold particles are nanocrystals.

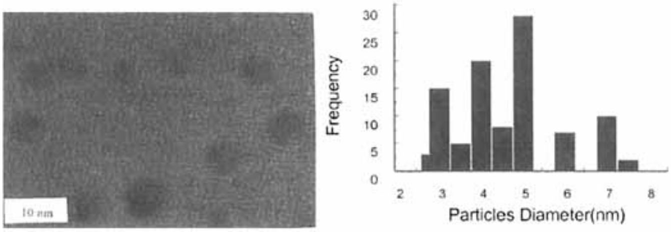
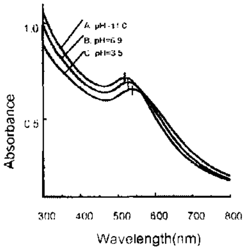


Figure 1 TEM image and size distribution of gold nanoparticles

The absorption spectra of MPA-capped gold nanoparticles in aqueous solution are shown in Fig. 2. The absorption band around 520nm is a characteristic of gold nanoparticles. It is attributed to the excitation of surface plasmon resonance and can be calculated from the Mie's theory[6a]. When the solution pH is changed from pH 11 to pH 3.5, a large red shift as well as a decrease in the absorption maximum is observed. This spectral change would not originate from precipitation. In the pH range explored, no discernible precipitation can be found for weeks, indicating good stability of the MPA-capped gold nanoparticles.



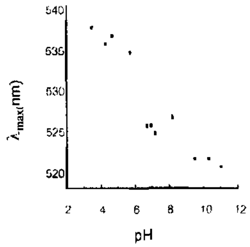


Figure 2(left) UV-Vis spectra of MPA-capped Au nanoparticles at different pH

Figure 3(right) pH-dependent absorption maximum wavelengths of the MPA-capped Au nanoparticles

Figure 3 shows the relationship between the absorption maximum wavelength and the pH of gold nanoparticle solutions. Obviously, with the decrease of pH, the wavelength of the absorption maximum gradually redshifted from 520 to 537 nm. This observation is consistent with that of Sastry [5] and Henglein[6b] on silver colloids. They attributed the redshift to the flocculation of nanoparticles. It is not true for our case, because we could not find any absorption band around 700nm, which indicates the flocculation of gold nanoparticles. We believe that the redshift observed here arises from the change of the dielectric environment of the nanoparticles, due to the different charging states of surface -COOH groups at different pH.

From Mie's theory, the surface plasmon band is produced by the collective excitation of free electrons in nanoparticles. The electric field vector of the incident light will influence the movement of free electrons, leading to a dipole excitation across the particle sphere. The dependence of the plasmon frequency (ω_p) on the free electron density allows for a simple explanation for our observation. At high pH, the -COOH groups are dissociated, leading to a larger negative charge density. This will increase the electron density of the nanoparticles, resulting in higher plasmon resonance frequency.

In summary, we have developed a simple, reproducible method to synthesize the gold nanocrystals capped with -COOH groups. This method can be extended to prepare nanocrystals capped with other bifunctional thiols. We also demonstrated that the optical properties of the MPA capped gold nanoparticles can be regulated by varying the pH of the solution.

Acknowledgment

Financial support from the National Natural Science Foundation of China(Grant No. 29803002) is gratefully acknowledged.

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