Super Stability of Ag Nanoparticle in Crystalline Lamellar (Lc) Liquid Crystal Matrix at Different pH Environment

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Abstract: The symmetry concept in this paper is related to the natural self-assembly of noble metal nanoparticles in the long range periodic structure of liquid crystal (LC). The current study deliberates the effect of pH on the stability of nanoparticles (NPs) in the lamellar phase of a lyotropic LC environment. The LC was prepared by the mass ratio 0.33:0.22:0.45 for (HDTABr):1-pentanol:water. The LC containing silver nanoparticles (AgNPs) was prepared by replacing the water with Ag solution. The AgNPs were produced by the in situ preparation method in LC. The solution of AgNPs-LC was varied at different pH. The absorption intensities were determined by using ultra-violet spectroscopy (UV-vis). The surface potential and hydrodynamic particle size were determined by using Zeta-potential (measurements). The surface enhanced Raman spectroscopy (SERS) was carried out to enhance the Raman signals of 4-aminobenzenethiol (4-ABT) deposited onto AgNPs as substrate. It is found that all characterizations exhibited super stability for AgNPs dispersed in LC at pH = 3 to 12 with the optimum stability at pH = 5–6. The remarkable stability of NPs is an important indicator of the various applications in nanotechnology and nanoscience fields.

Keywords: silver nanoparticle; liquid crystal; zeta potential; SERS; 4-aminobenzenethiol

1. Introduction

Extensive achievements have been made in display materials since the 1970s involving the famous material such as liquid crystal (LC), leading to manufacturing of outstanding organic light emitting displays (OLEDs). With the rapid development and achievements over the last decade, many researchers moved their exploration to the new era of LCs applications such as biosensors [1], robotics, telecommunications and nano-manipulation [2].

Simultaneously, the revolution of nanotechnology and nanoscience lead to a series of nanostructured materials below 100 nm size earning vast attention in academic and industrial sectors. Due to size-dependence and the greatness of the optical, chemical and electromagnetic properties of nanostructured materials, they have attained remarkable significance in contrast to their counter bulk parts, providing a large surface area and excellent thermal and electrical conductivity [3]. Nanostructured materials have found applications in a diverse range of nanoscience and nanotechnology fields ranging from bio to medical, catalysis, optics, cosmetics, energy, health and electronics [4–9] to name a few.

A new material has been composed by inclusion of nanomaterial to a LC material, which is expected to act differently to their solo element either on a macroscopic or microscopic scale. The hybrid
of LCs-nanomaterials can modify the original chemical and physical properties of LCs. It can also modify the nanomaterial properties by manipulating and ordering LCs that can obtain additional benefits from LCs or nanomaterials themselves for their new state and properties [2].

In that case, both main types of LCs, thermotropic and lyotropic, can be considered as a medium for the preparation of nanomaterials or as a reaction medium [10], or stabilizing agent [11] and act as a template for nanomaterials with desired morphology [12]. LCs can also play as regulator for nanomaterial growth because of their exceptional self-assembling behavior that have long-range ordering and can be mobile at the nanoscale level [13].

Several observations of the hybrid noble metal nanoparticle in LC have been reported to study particle size, morphology and possible growth of gold and silver nanoparticles by using hexagonal and lamellar phases of lyotropic LCs [13]. The stability of silver nanoparticle is investigated in lamellar LCs by the way of ex-situ and in-situ methods [14], observing the effect of temperature, composition and ageing on the ribbon of silver nanoparticles synthesized in lamellar LCs with C12E4 as a surfactant itself as reductant [15]. The dispersion state and stability of a hybrid system of hydrophilic and hydrophobic silver nanoparticles existing in an aqueous layer and organic region of the surfactant lamellar phase was investigated by Wong et al. [16].

Due to the valuable works mentioned above, we made an attempt to study a hybrid system of noble metal nanoparticles in LCs stability under variations of pH solution. Before conducting measurements, we looked for previous reports that described an interpretation of how the pH solutions affect the silver nanoparticles’ stability in any medium. Ishara and Yan [17] synthesized uncoated silver nanoparticles by chemical reduction method using silver nitrate and sodium borohydride. They varied the nanoparticles colloidal in acidic and basic solution in pH range of 5–8 and found that the nanoparticles size decreased when pH values increased. A lower aggregation rate resulted in particle stability increasing, while different situation for nanoparticles in acidic and neutral solution were destabilized with an aggregation occurring at a higher rate. Nazar and co-workers [18] reported that the effect on the stability of gold and silver nanoparticles were biosynthesized using *Prunus armeniaca* fresh gum, in a pH range of 2–13. Both exhibited instability due to the aggregation in the basic medium which increases particle size but stable in acidic medium. Accordingly, pH involves a necessary part on stable nanoparticles formation and nanoparticles redispersion.

In this study, we chose self-assembling organic lyotropic LCs to generate silver nanoparticles and attached them in patterned arrays within lamellar layers. The lamellar phase can act as a soft confinement for long range periodicity and as the control medium for nanoparticles nucleation and growth process [19]. The assembly of noble silver nanoparticles into well-defined arrays offer unique and tunable optical properties as the occurrence of surface plasmon resonance (SPR) provides possibilities of new potentially collective phenomena.

The stability and agglomeration tendency of colloidal nanoparticles can be understood via the classical Derjaguin, Landau, Verwey and Overbeek (DLVO) theory that considered electrostatic repulsion and attractive van der Waal’s interaction between particles [20]. The particles that are surrounded by a diffuse electrostatic double layer (EDL) will be dispersed when the repulsion can overcome the attractive force. The repulsion force is induced by a similar electrical charge (positive-positive or negative-negative) surrounding the particles. The magnitude of the electrical surface charge and the electrostatic double layer are related to the pH, and ionic strength plays an important role in the colloidal stability. Besides, noble metal nanoparticles may affect the spectroscopic Raman signal which can induce morphological coupling between absorption and scattering simultaneously [21,22]. In this regard, we manifested the nanostructured silver nanoparticles present as a substrate to SERS activity at different pH environment according to their strong durability and wide SPR in visible and near infrared regions.
2. Materials and Methods

Silver nitrate (AgNO$_3$), sodium borohydride (NaBH$_4$), hexadecyltrimethylammonium bromide (HDTABr, 98%, powder), 1-pentanol (99%) and 4-Aminobenzenethiol (4-ABT, 97%) were purchased from Sigma Aldrich. Preparation of:

(i) **Pure LC.** The solution of HDTABr:1-pentanol:water was prepared by the mass ratio of 0.33:0.22:0.45.

(ii) **LC containing AgNPs (LC-AgNPs).** In this case, the AgNPs were produced by an in situ method in the LC system. Firstly, the mixture of HDTABr:1-pentanol was prepared by the mass ratio of 0.33:0.22. Then 0.01 M AgNO$_3$ solution and 0.04 M NaBH$_4$ solution in a volume ratio 1:1 were added to the HDTABr:1-pentanol mixture. The specific components ratio of HDTABr:1-pentanol:water (or Ag solution) was referred to in the ternary diagram illustrated earlier by Patakfalvi et al. [14] that also stated that AgNPs content, using this method, is 0.005 M.

Then, the system in (i) and (ii) was left for one day at room temperature to develop the LC structure. The LC phase texture was observed with a polarizer microscope (POM). The physical size and shape of nanoparticles were determined by using a Zeiss LEO LIBRA 120 high resolution transmission electron microscopy (HRTEM).

For evaluation of stability, the effect of pH on the solution of AgNPs-LC was studied. The samples were prepared in small glass containers. The pH was adjusted by adding drop wise 1 M HCl or NaOH solution for pH = 1–2, 3–4, 5–6, 7–8, 9–10, 11–12 and 13–14. All samples were kept at room temperature for one day before measurement.

Absorption spectra were recorded in the 600–300 nm region at room temperature with a Cary 50 Probe UV-Visible Spectrophotometer (UV-Vis). The zeta potential, zeta average and size distribution were determined by a Malvern Zetasizer Nano ZS. Prior to the measurements, the samples were diluted by distilled water 15-fold. SERS was prepared by a 1.0 mM 4-ABT solution dropped onto 5 mM LC-AgNPs solution earlier deposited onto a glass slide by covering an approximate area of 0.25 cm$^2$ and left to dry for one day at room temperature. The measurements were carried out by using a Horiba Sientific-Xplora Olympus BX41 with a 532 nm green laser.

3. Result and Discussion

Lamellar LCs phases before and after being introduced to AgNPs are shown in Figure 1a,b. The images represents HDTABr:1-pentanol:water and HDTABr:1-pentanol:AgNPs solution by the same composition of 0.33:0.22:0.45. The focal conic like fan shape texture [23] formed for both images. This may be due to the low surfactant:cosurfactant ratio. The multiple layers interlace with some oily streaks observed in the phase of lamellar LCs with AgNPs.

Figure 1c sketches the lamellar bilayers. Each bilayer constitutes two monolayers arranged head to head (hydrophilic part) and they shield water from contact with the hydrophobic region. The structure can exhibit short range and long range ordering and a type of lamellar phase known as crystalline lamellar (L$_c$) [24]. According to Patakfalvi et. al. [14] the lamellar distance, $d_{Lc}$, of the volume composition 0.33:0.23:0.45 was 3.92 nm. Since their composition system is similar to current study thus it is assumed that there is similar lamellar distance.

The image and particle size distribution of AgNPs dispersed in the LC medium at room pH = 7–8 are shown in Figure 2. The average NPs size is 4–5 nm with a narrow size distribution and in a spherical shape. The NPs sizes is slightly larger than expected $d_L$. The tendency of NPs aggregation may be high according to it not being incorporated and trapped evenly in the lamellar layer. However, the stability of NPs can be monitored by controlling pH from an acidic to a basic environment. This was agreed with by Badawy et al. [25]; pH plays an important role in synthesis and stabilization of NPs dispersion after being completely formed.
The SPR peak shows a maximum peak slightly shifting to a longer wavelength, 404 nm and larger layer were not aggregated and revealed the particles were stable in a wide pH range. While at pH obtained at 403 nm and 41.65 respectively, as detailed in Table 1. The AgNPs trapped in the lamellar structure constitutes amphiphile stack bilayers. Since it is without AgNPs and there are single bands with a narrow Gaussian shape in a range of 5 to 12 no di different peak location and maximum width was monitored by measuring the SPR bands in different pH solutions. Figure 3 shows a visible region with a non-absorption peak for an LC sample since it is without AgNPs and there are single bands with a narrow Gaussian shape in a range of pH = 3 to 12. The physical size of generated AgNPs is estimated to be less than 20 nm with a spherical shape [26].

In the middle pH range (pH = 5 to 12) no different peak location and maximum width was obtained at 403 nm and 41.65 respectively, as detailed in Table 1. The AgNPs trapped in the lamellar layer were not aggregated and revealed the particles were stable in a wide pH range. While at pH = 3–4, the SPR peak shows a maximum peak slightly shifting to a longer wavelength, 404 nm and larger bandwidth. This situation described how and when AgNPs dispersed in a higher acidic medium. It may cause an aggregation tendency and exhibit slight instability.
Figure 3. Absorption spectra of liquid crystal (LC)-AgNPs at various pH.

Table 1. Characteristic of AgNPs disperse in LC medium at various pH.

| LC-AgNPs (pH) | Wavelength, λ (nm) | Absorption | FWHM (nm) | Z-Average, d (nm) | Z-Potential, ζ (mV) | Polydispersity Index, PdI |
|---------------|--------------------|------------|-----------|-------------------|---------------------|------------------------|
| 1–2           | -                  | -          | -         | 40.00             | 36.0                | 0.55                   |
| 3–4           | 404                | 0.22       | 46.65     | 44.39             | 68.6                | 0.55                   |
| 5–6           | 403                | 0.80       | 41.65     | 39.30             | 70.7                | 0.53                   |
| 7–8           | 403                | 0.80       | 41.65     | 45.04             | 69.0                | 0.53                   |
| 9–10          | 403                | 0.72       | 41.65     | 43.98             | 65.9                | 0.53                   |
| 11–12         | 403                | 0.68       | 41.65     | 43.82             | 52.5                | 0.53                   |
| 13–14         | -                  | -          | -         | 722.97            | 36.0                | 0.43                   |

In extreme acidic and alkaline environments, there are no SPR bands observed. The AgNPs may experience incompatibility with the absorption activity due to the changes in their state, surface charge and morphology. The formation of an oxide layer onto the AgNPs’ surface may be possible at a low pH due to the impact of the dissolution oxidation process and silver nanoparticles may turn to silver oxide (Ag₂O) [17]. While highly alkaline, precipitation of nanoparticles may occur [27]. This is due to the uncontrolled aggregation when the hydroxyl ions were introduced to the colloidal system.

Figure 4a shows the histogram of zeta potential, ζ at various pH. The change in pH affected the surface potential of AgNPs dispersed in LC. In the whole pH range, all ζ values exceeded a minimum of ±30 mV indicating the LC medium has a good colloidal nature that supports the AgNPs’ stability. The high value of ζ due to the preferential adsorption of H⁺ greater than OH⁻ ions provided the sufficient positive-positive repulsion to remain stable in solution [3,28]. The maximum of ζ + 70.7 mV at pH = 5–6, indicates the strongest interaction between the freshly prepared AgNPs and the surrounding LC. The H⁺ actively attached to the stern layer and continued to attract the diffuse layer or electrical double layer at the AgNPs’ surface.

In high basic pH = 13–14, the ζ represented electrical potential at the slipping plain between AgNPs’ surface and their medium, decreased to +36.0 mV. The high content of hydroxide ions may alter the EDL to lower potential resulting in a weaker repulsion force among nanoparticles. The aggregation
kinetics were accelerated and caused AgNPs’ stability to decrease, resulting in a large NPs size. The potential also decreased at low acidity to +36.0 mV that means the stability of NPs is in the lower state due to the particles’ dissolution according to the oxidation mechanism. However, in the destabilization process, the potential values at high acid and alkaline still exceeded the minimum value of ζ indicating a strong electrostatic repulsive interaction exists between lamellar–lamellar, Ag–Ag and Ag–lamellar.

Figure 4. (a) Zeta potential and (b) zeta average of LC‐AgNPs at various pH. Size distribution of (c) pH = 5–6 and (d) pH = 13–14.

The zeta average \(d\) gives a mean particle size (hydrodynamic size) [29], which is not obviously affected by variation of pH unless for high basic as displayed in Figure 4b. The polydispersity index (PDI) estimates the width of the particle size distribution with 0 of PDI representing the high monodisperse while 1 represents broad polydisperse distribution [29]. PDI values all over the range of pH were found above 0.5 but not for high basic exhibited in the lower index, as detailed in Table 1. Figure 4c shows the size distribution curve for pH = 5–6 (represent for all samples) in a polydisperse distribution, while pH = 13–14 was monodisperse in nature as shown in Figure 4d.

Figure 5 shows that the molecule of 4-ABT and the LC-AgNPs have been used as a substrate to enhance the Raman signal. The molecule of the analyte was adsorbed onto the surface of Ag through the sulphur atom by splitting of the S–H bonding. According to Shin et.al. [30] that normal Raman spectra of 4-ABT in neat solid state has two strong peaks at (i) 1087 cm\(^{-1}\) and (ii) 1593 cm\(^{-1}\) and both represent a \(\nu_{CS, (7a)}\) and \(\nu_{CC, (8a)}\), respectively [31].

The pH effectiveness of LC-AgNPs substrate is recognized by measuring the Raman signal of 4-ABT as shown in Figure 6. The five strong peaks appear at acidic pH = 5–6 spectrum. The peak locations are 1566, 1426, 1388, 1141 and 1076 cm\(^{-1}\) with their assignations being 8a, 19b, 3, 9b and 7a, respectively, which are in good agreement with a previous study [32]. The assignation detail for the other pH spectrum can be recognized in Table 2. It can be deduced from the figure that the spectral features depend on the measurement condition but this is not the case for substrate dependence and excitation wavelength.
The $a_1$ exhibited EM enhancement when the molecule of the analyte was adsorbed onto AgNPs surface roughness and the $b_2$ bands affected by chemical enhancement [31]. According to Kim et al. [33] that signature of the strong $b_2$ symmetry vibration intensity borrowed from an intensity of $\pi \rightarrow \pi^*$ molecular transition. The molecules of 4-ABT were affected in the middle range of pH. The most influenced occurred at pH = 5–6 exclusively induced by EM and chemical enhancement. The boosting of the 4-ABT molecule was also adsorbed due to the decrease in AgNPs size. This was related to the reducing gap among NPs which acted as a substrate and can induce the strong SERS intensity [34].

The LC-AgNPs roughness feature produced a heterogeneous layer consisting of the orientating characteristic of the particles which is advantageous for producing the magnitude of the Raman signals. The relatively low intense SERS signals at high basic is due to the high volume of NAOH (anions, $\text{OH}^-$), which increases the surface coverage of the adsorbent. The $b_2$ bands of 4-ABT disappear at low pH due to protonate of the amine group inducing a gap in the blue shift between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, thus hindering the charge transfer resonance chemical enhancement mechanism in SERS.
4. Conclusions

In this study, we have successfully prepared AgNPs using an in situ method in the lamellar lyotropic LC medium. The crystalline lamellar (Lc) phase obtained in a streaky or mosaic like pattern. The physical size AgNPs dispersed in LC is 2–8 nm. We practically varied the pH to monitor the stability of particles incorporated within the lamellar layer.

At pH = 5 to 12, the absorption characteristic showed that the AgNPs are not aggregated when highly dispersed. The super stability in this wide pH range was verified by high positive $\zeta$ values indicating that colloidal nanoparticles dispersed in a strong electrostatic stabilization environment. Hence, their kinetic level of nanoparticle aggregation is slow. The hydrodynamic sizes were not too distinguished while the dispersity indexes were specified above 0.5, proving nanoparticles were in a polydispersed distribution. The electromagnetic and chemical interactions were enhanced in SERS activity with the most apparent the a1 type bands.

At pH = 3–4, the absorption characteristic of AgNPs slightly red shifted, which clarified nanoparticles that are slightly agglomerated indicating less stability in a more acidic environment. This was supported by the $\zeta$ value decreasing, while their size was also not too distinguished. At a low pH, no SPR band was detected and the $\zeta$ value continually decreased due to the dissolution nanoparticle. The Raman signal was shown to be ineffective in highly acidic conditions. Meanwhile, at high alkaline, the SPR band was also non-existent due to the nanoparticles being in an enormous agglomeration. In this stage, the kinetic behaviors are very fast. The $\zeta$ value decreased, which the NPs carried out with less stability and their hydrodynamic size showed as prominent. A larger gap spacing among nanoparticles inhibited Raman signals’ boosting for the detection of 4-ABT characteristics.

We can say that the lamellar LC phase can be an important medium in controlling the self-assembly and self-organization of AgNPs and a stabilizer medium in a wide pH range (lower acid to higher basic). At the same time, the variety of pH necessitated stable nanoparticle formation, nanoparticle dissolution and agglomeration kinetics. Many applications could be encouraged through this work based on the unique AgNPs’ physicochemical properties making them valuable in many areas such as medicine, catalysis, industrial demand and also in scientific investigation and in metamaterial approaches.

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Table 2. Vibrational assignment of 4-ABT in AgNPs substrate.

| Normal Raman | SERS (cm$^{-1}$) | Assignment |
|--------------|-----------------|------------|
| pH = 1–2     | 1583, 1518      | $\tilde{v}$CC, (8a) |
| pH = 3–4     | 1526, 1526, 1560, 1560, 1560, 1560, 1560 | $\tilde{v}$CC, (8b) |
| pH = 5–6     | 1526, 1510, 1510, 1510, 1510, 1510, 1510 | $\tilde{v}$CC, (19a) |
| pH = 7–8     | 1526, 1522, 1522, 1522, 1522, 1522, 1522 | $\tilde{v}$CC, (19b) |
| pH = 9–10    | 1526, 1522, 1522, 1522, 1522, 1522, 1522 | $\tilde{v}$CC, (3) |
| pH = 11–12   | 1526, 1522, 1522, 1522, 1522, 1522, 1522 | $\tilde{v}$CC, (9a) |
| pH = 13–14   | 1526, 1522, 1522, 1522, 1522, 1522, 1522 | $\tilde{v}$CC, (9b) |

Denoting st-strong, me-medium, we-week, vwe-very weak, `stretch, $\tilde{v}$-bend, a1(8a,7a), b1(8b), b2(19b,9b,3).
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