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# Understanding the Dichroic Effect of Silver Nanoparticles Synthesized by a Chemical Reduction Method

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**Abstract** During our study of the synthesis of metal nanoparticles via chemical reduction methods, we found that some colloidal solutions of silver nanoparticles displayed dichroic effect. The dichroic effect is a phenomenon where a material displays two different colors in transmitted light and reflected light. In this study, dichroic silver nanoparticles were obtained via a simple chemical reduction method under ambient conditions. Ascorbic acid was used as the reducing agent and trisodium citrate was used as the stabilizing agent. A colloidal solution of synthesized silver nanoparticles showed an opaque gray color in reflected light and a translucent pink color in transmitted light. Another colloidal solution prepared in the presence of copper (II) sulphate displayed a new combination of dichroic colors: opaque blue and translucent green. To understand the formation of dichroic effect, Transmission electron microscopy (TEM) and UV-Vis spectroscopy were used to characterize and study the silver nanoparticles in these colloids. TEM study showed that silver nanoparticles with different sizes and shapes were present in the solutions that displayed dichroic effect. By comparing the morphology of dichroic silver nanoparticles with that of the silver nanoparticles that exhibited no dichroic effect, we concluded that both the sizes and the shapes of nanoparticles play important roles in the formation of dichroic effect. The small particles are responsible for the absorbance of light, which results in the color in transmitted light. While large particles account for the scattering of light and lead to the color in reflected light. Different combinations of nanoparticles with different sizes and shapes lead to different colors for the dichroic effects

***Keywords:*** *silver nanoparticles, dichroic effect, chemical reduction method, UV-Vis, TEM*

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## 1. Introduction

Because of their extraordinary physical, chemical, optical, mechanical, magnetic, and biomedical properties, metal nanoparticles have attracted great research interests in the past decades. Extensive applications of metal nanoparticles have been found in various fields such as catalysis [1,2,3,4], energy storage [5], biomedical sciences and engineering [6,7,8]. The integration of the well-established properties of metal nanoparticles with the emerging nanotechnology opens a new dimension in materials science [9].

The synthesis of metal nanoparticles is an active research area in nanoscience. Current methods for the synthesis of metal nanoparticles can be classified in to three categories: physical methods, chemical methods, and biological methods [10-13]. Evaporation-condensation and laser ablation are the most used physical approaches. Chemical methods usually include chemical reduction, radiolysis, and electrochemical techniques. Biosynthesis of metal nanoparticles uses non-toxic biomaterials such as bacteria, yeast, algae, and plant extracts. Therefore, biological methods are often referred to as green methods.

Among the metal nanoparticles, silver nanoparticles have formed as one of the largest and fastest growing groups and received numerous research attention due to their unique chemical, physical, electrical, antibacterial, and optical properties [14]. During our study in the synthesis of metal nanoparticles by chemical reduction methods, we found that a colloidal solution of silver nanoparticles synthesized by the reduction with ascorbic acid in the presence of trisodium citrate showed an interesting dichroic phenomenon: two different colors were observed in transmitted light and reflected light. An impressive example of the dichroic property of metal nanoparticles is the ancient glass artefact, Lycurgus cup from the 4$^{th}$ century, which showed a red color in transmitted light and a green color in reflected light [15]. In optics, a dichroic material absorbs one plane-polarized light component more strongly than the other. Due to this special optical property, dichroic materials have been utilized in various fields such as dichroic polarizer [16,17], LCD devices [18], and sensors [19,20]. Although the dichroic effect observed in metal nanoparticles has been described several times [21,22,23,24], the explanations for the origin of dichroic effect in metal nanoparticles haven't reached an agreement yet. Some researchers think this phenomenon depends on the presence of highly polymorphic nanoparticles [25], some attribute it to the presence of specific shapes of nanoparticles [22] or bimodal size distributions [26], while other researchers conclude the source of the dichroic effect only links to the particle size with no special particle shapes or size distribution required [27]. More research is needed to expand the knowledge on the source of dichroic effect of metal nanoparticles. Here, we report our point of view for the cause of dichroic effect in silver nanoparticles synthesized by a simple, one-pot chemical reduction method under ambient conditions.

## 2. Materials and Methods

### 2.1. Materials

Silver nitrate (99%), citric acid trisodium salt (98%), copper (II) sulfate pentahydrate (98%), sodium borohydride (99%), were purchased from Sigma-Aldrich. Ascorbic acid (reagent grade) was purchased from Fisher Science Education. All chemicals were used as received without further purification.

### 2.2. Methods

#### 2.1.1. Synthesis of Dichroic Silver Nanoparticles

Dichroic colloidal solution were obtained during the synthesis of silver nanoparticles by the chemical reduction with ascorbic acid in the presence of trisodium citrate under ambient conditions. The procedure of the synthesis was as follows: first, dissolve 0.4 mmol of trisodium citrate in 100mL of distilled water in a 125 mL Erlenmeyer flask. Then 0.1 mmol of silver nitrate was added to the solution of trisodium citrate with stirring. After silver nitrate completely dissolved, 2mL of aqueous solution of ascorbic acid (0.05 M) was added dropwise. The reaction mixture was continuously stirred at room temperature. UV-Vis spectroscopy was used to monitor the formation of silver nanoparticles.

#### 2.1.2. Synthesis of Dichroic Silver Nanoparticles in the Presence of Copper (II) Sulfate

Another dichroic colloidal solution was seen with a new combination of colors when copper (II) sulphate ($CuSO_4$) was introduced into the synthesis. First, dissolve 0.4 mmol trisodium citrate in 100mL of distilled water in a 125 mL Erlenmeyer flask. Then 0.1 mmol of $CuSO_4$ was added to the flask while stirring. After $CuSO_4$ was completely dissolved, 0.1 mmol of silver nitrate was added to the flask. After silver nitrate was completely dissolved, 2mL of aqueous solution of ascorbic acid (0.05 M) was added dropwise. The reaction mixture was continuously stirred at room temperature until no significant change in the absorbance of UV-Vis spectrum was observed.

#### 2.1.3. Synthesis of Silver Nanoparticles by Using Sodium Borohydride as the Reducing Agent

To do a further comparison study, silver nanoparticles were synthesized with a strong reducing agent, sodium borohydride ($NaBH_4$) under similar conditions. First, dissolve 0.4 mmol of trisodium citrate in 100mL of distilled water in a 125 mL Erlenmeyer flask. Then 0.1 mmol of silver nitrate was added to the flask while stirring. After silver nitrate was completely dissolved, 1mL of aqueous solution of $NaBH_4$ (0.1 M, freshly prepared) was added dropwise. The reaction mixture was continuously stirred at room temperature. UV-Vis spectroscopy was used to monitor the formation of silver nanoparticles.

## 3. Results

### 3.1. UV-Vis and TEM Study of Silver Nanoparticles with Dichroic Effect

The mystery of the Lycurgus cup was solved in 1990 when scientists discovered a mixture of silver and gold nanoparticles in the glass matrix [28]. During our study, when silver nitrate was reduced by ascorbic acid in the presence of trisodium citrate, the colloidal solution of the resulted silver nanoparticles displayed dichroic effect: an opaque gray color under reflected light and a translucent pink color in transmitted light (Figure 1). Trisodium citrate is a very weak reducing agent and when used, it is often used under boiling conditions [29]. Here, trisodium citrate was chosen with the following functions. First, it was used as a stabilizing agent in particle growth. Secondly, it helped enhance the reduction power of ascorbic acid at room temperature [30].

**Figure 1.** Dichroic colloidal solution of silver nanoparticles in reflected light (left) and transmitted light (right)

The UV-Vis spectrum of the prepared solution showed a broad peak with $\lambda_{max}$ at 445 nm, which is the surface plasmon resonance (SPR) absorption of silver nanoparticles (Figure 2). SPR is the result of coherent excitation of the free electrons in the surface of metal nanoparticles and their in-phase resonance with incident light. The SPR band can be influenced by the size, shape, and polydispersity of nanoparticles and surrounding medium of nanoparticles [23]. The broad SPR band in

Figure 2 indicates the presence of polydisperse silver nanoparticles. Ascorbic acid is a mild reducing agent at room temperature. According to the nucleation theory on the formation of nanoparticles, its seed formation rate is relatively slow. The slow nucleation rate will lead to broad size distribution of nanoparticles. On the other hand, the presence of sodium citrate gives rise to the formation of anisotropic silver nanoparticles by the preferential binding to certain crystal facets (Ag {111}) [31], which results in broad SPR band as well. TEM image confirmed the presence of polydisperse nanoparticles, mainly spherical and quasi-spherical nanoparticles (Figure 3).

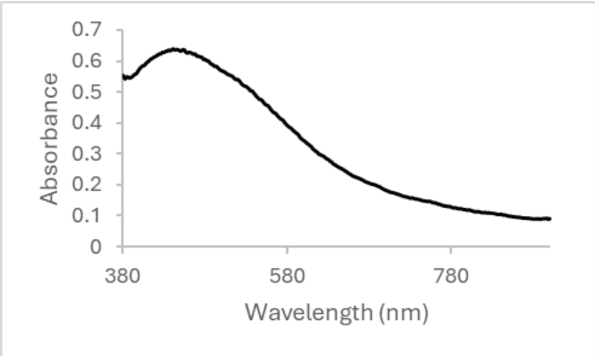


**Figure 2.** UV-Vis spectrum of colloidal solution of silver nanoparticles with dichroic effect

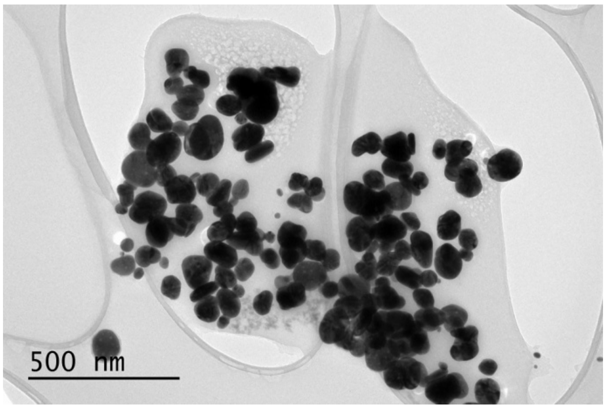


**Figure 3.** TEM image of dichroic silver nanoparticles

**Figure 4.** Dichroic colloidal solution of silver nanoparticles formed in the presence of $CuSO_4$ in reflected light (left) and transmitted light (right)

In another experiment, when $CuSO_4$ was introduced to the reaction mixture before the addition of silver nitrate, the final prepared solution displayed a new combination of dichroic colors, an opaque blue color in reflected light and a translucent green color in transmitted light (Figure 4). The UV-Vis spectrum of the prepared solution showed two broad peaks, with $\lambda_{max}$ at 425 nm and 675 nm respectively (Figure 5).

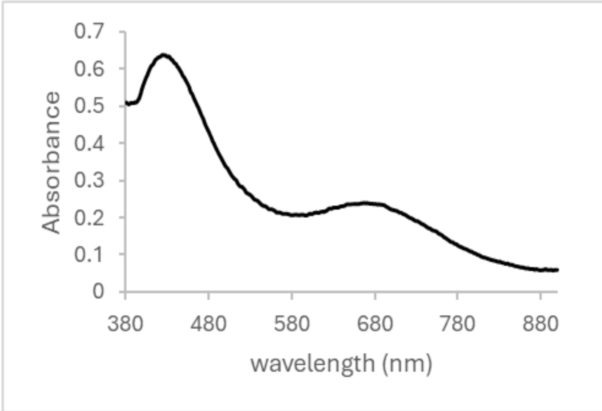


**Figure 5.** UV-Vis spectrum of prepared solution of dichroic silver nanoparticles formed in the presence of $CuSO_4$

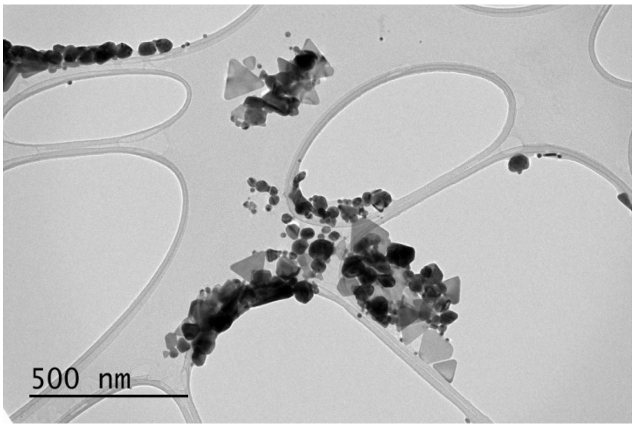


**Figure 6.** TEM image of dichroic silver nanoparticles formed in the presence of $CuSO_4$

The broad peak with $\lambda_{max}$ at 425 nm implies the presence of polydisperse spherical and quasi-spherical nanoparticles, as those observed in previous sample. The presence of a second broad peak at 675 nm in the UV-Vis spectrum indicates the presence of nanoparticles with a new shape and size distribution. TEM image of the prepared solution showed, except for the spherical and quasi-spherical nanoparticles, triangular nanoparticles with different sizes were present in the solution as well (Figure 6). The large size distributions agree with the broad peak width. Similar optical property has been observed by other researchers and the second peak at the longer wavelength was linked to the triangular silver nanoparticles [23].

Based on the UV-Vis and TEM study, we assume that the presence of polydisperse nanoparticles with different shapes is the source of dichroic effect. To prove this conclusion, we did a further comparative study of silver nanoparticles that did not display dichroic effect.

## 3.2 UV-Vis and TEM Study of Silver Nanoparticles with no Dichroic Effect

To understand the formation of dichroic effect, under the same ambient conditions, $NaBH_4$ was used as the reducing agent to replace ascorbic acid. The prepared colloidal solution didn't display the dichroic effect. UV-Vis spectrum of the yellow colloid showed a narrow SPR band with $\lambda_{max}$ at 400 nm, which is the characteristic absorption of spherical silver nanoparticles (Figure 7).

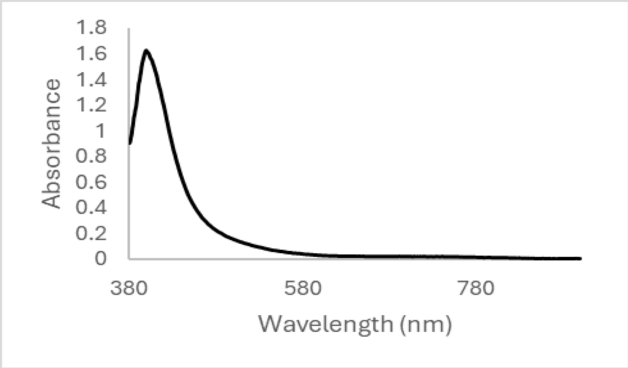


**Figure 7.** UV-Vis spectrum of the colloidal solution of silver nanoparticles with no dichroic effect

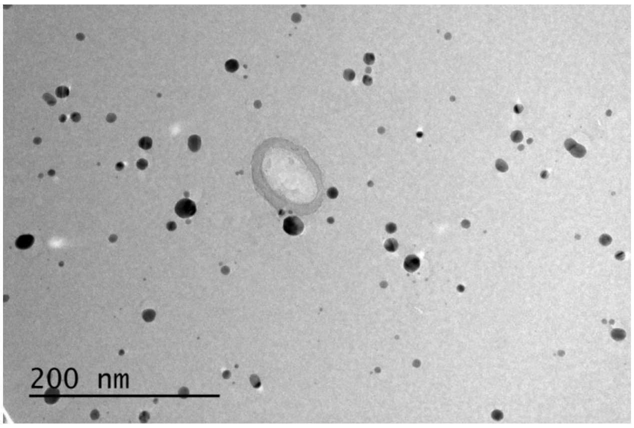


**Figure 8.** TEM image of silver nanoparticles with no dichroic effect

TEM image showed that the colloid with no dichroic effect contained small spherical particles (< 20 nm) with narrow size distribution (Figure 8), which matches the sharp narrow SPR band in the UV-Vis spectrum. The UV-Vis and TEM study of the nanoparticles with no dichroic effect confirmed our assumption that the presence of polydisperse nanoparticles with different shapes is the source of dichroic effect.

In another study for the synthesis of silver and gold alloy nanoparticles, we obtained a colloidal solution with an orange-brown color. TEM image showed the solution contained nanoparticles with different shapes. The sizes of the nanoparticles are less than 20 nm. This solution didn't show dichroic effect either (Figure 9).

According to the study by El-Sayed and co-workers based on the Mie theory, the optical absorption and scattering properties of metal nanoparticles depend on the sizes and shapes of nanoparticles [32,33]. In their study, with metal spherical nanoparticles less than 20 nm, no scattering was shown. This explains why the silver nanoparticles synthesized with $NaBH_4$ didn't show a different color in reflected light. When the size of metal nanoparticles increased to 40 nm in their study, the scattering of light started to be observed. As the size of nanoparticles continued increasing, the Mie scattering increased and eventually resulted in opaque reflection. Therefore, we believe the opaque reflection observed in the colloids of dichroic silver nanoparticles in our study are due to the scattering of light by large nanoparticles and the colors in transmitted light are attributed to the absorbance of light by small nanoparticles. Besides, the composition ratio of nanoparticles with different shapes determines the colors of the solutions in reflected light and transmitted light.

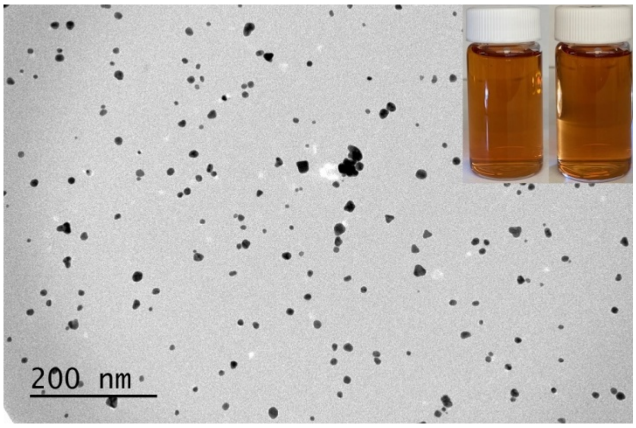


**Figure 9.** TEM image of a mixture of silver and gold nanoparticles. The inset shows the corresponding colloidal solution in reflected light (left) and transmitted light (right)

In the synthesis of metal nanoparticles by chemical reduction methods, several chemicals are required and each of them plays a specific role such as metal precursor, reducing agent, stabilizing agent, etc. To understand the effect of each reactant in our synthesis method on the morphologies of the nanoparticles and their optical properties, more detailed studies on these factors are in progress.

## 4. Conclusion

During our study of the synthesis of metal nanoparticles via chemical reduction methods, dichroic colloids of silver nanoparticles were obtained under ambient conditions. Ascorbic acid was used as the reducing agent and trisodium citrate was used as the stabilizing agent. A colloidal solution of synthesized silver nanoparticles showed an opaque gray color in reflected light and a translucent pink color in transmitted light. Another colloidal solution prepared in the presence of $CuSO_4$ displayed a new combination of dichroic colors: opaque blue and translucent green. To understand the formation of dichroic effect, TEM and UV-Vis spectroscopy were used to characterize and study the silver nanoparticles in these colloids. TEM study showed that silver nanoparticles with different sizes and shapes were present in the colloidal solutions that displayed dichroic effect. By comparing the morphology of dichroic silver nanoparticles with that of the silver nanoparticles that did not display dichroic effect, we concluded that both the sizes and shapes of nanoparticles play important roles in the formation of dichroic effect. The small nanoparticles are responsible for the absorbance of light, which results in the color in transmitted light. While large nanoparticles account for the scattering of light and lead to the color in reflected light. Different combinations of nanoparticles with different sizes and shapes determine the colors of the solutions in reflected light and transmitted light.

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