SYNTHESIS AND GROWTH OF SILVER NANOCRYSTALS IN NATURAL RUBBER MATRIX

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ABSTRACT

Silver (Ag) nanoclusters in natural rubber (NR) matrix were prepared. Silver ions were reduced by means of a UV light. The matrix in which the silver clusters were synthesized were both in the form of a film as well as a colloid solution. The morphology of the silver clusters was studied in both systems. Investigations showed that silver nanoparticles were obtained in the natural rubber films while silver fractals and nanoparticles coexisted in the colloidal solution. The products were characterized using Transmission Electron Microscopy (TEM) and X – ray Diffraction (XRD).

Keywords : *Silver nanoparticles; Silver fractals; Morphology; Natural rubber; UV irradiation.*

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1. Introduction

Noble metal nanoclusters have been investigated extensively due to its significant properties, which differ greatly from its bulk material as well as its wide scope of applications. It has attracted considerable interest in various fields such as optics[1-3], catalysis[4-5] and electronics[6]. These properties are dependent on the morphology of the nanoclusters obtained and as such, much attention has been paid to synthesizing clusters with different shapes and sizes. Recently, the formation of various nanostructures has been studied including nanowires[7], dendrites and fractals[8-9], nanoparticles[10-11] and nanoprisms[12]. These materials can be obtained by varying experimental conditions. Hence, many methods have been reported such as chemical reduction[13-15], sonochemical techniques[16], gas evaporation [17], and radiation techniques[18-19].

An extensive range of metals has been studied. Among them, diverse investigations on synthesizing silver nanoclusters have been carried out. This is due to its importance in photographic science[20] as well as its application in catalytic activities. Besides that, silver is also important because of its selectivity for the epoxidation of alkenes[18] and other technological aspects.

Recently, the processing of nanosized silver in a variety of matrix has been emphasized. Polymers such as poly (vinylpyrrolidone) [8,21], poly (vinylalcohol) [22] and DNA[23] not only act as matrixes, but also as a colloidal stabilizer. The use of these polymers as well as the choice of chemical reductant or method indirectly affects the morphologies of metal nanostructures. As an example, a procedure reported by Xiuwen Zheng et. al.[24] has proven that when silver is reduced with ascorbic acid dendrites are formed. However, when KBH_4 is used as a reducing agent instead, silver nanoparticles are produced.

Natural rubber latex is of great importance in industries such as manufacturing tires and rubber gloves. Although it is widely used, extensive research has been conducted to change its properties not only to compete with synthetic rubber but also to broaden its applications. This is due to the increasing awareness towards environmental issues as well as the fact that this polymer is a renewable source.

In this paper, we report a novel method to synthesize silver nanoparticles and fractals by UV irradiation in a natural rubber matrix. The nanostructure of silver in natural rubber composite films were studied and compared to those formed in natural rubber latex. The silver nanoclusters were observed by transmission electron microscope (TEM) and characterized using X – ray diffraction (XRD). Size distribution of the silver nanoparticles was also obtained. The proposed mechanism that leads to the formation of both silver nanomaterials is also discussed.

2. Experimental

2.1 Materials and Preparation of Silver – Polymer Matrix

Natural rubber latex (NRL) with a dry rubber content (DRC) of 60% was supplied by BARD Malaysia Sendirian Berhad. The latex consisted of 7% ammonia which was used as a stabilizer and had a pH of 9. Silver nitrate ($AgNO_3$) was purchased from Johnson Matthey Material Technology U. K. and was used as received.

Clean NRL was used to prepare the samples. This was obtained by centrifuging the NRL at 5613g using a Kubota Model 5800 centrifuge. The cream phase was then separated and diluted to 30 % DRC using distilled water.

Following this, 1g of clean NRL was diluted with 20 ml of distilled water and added to 0.005g (2.94 x 10-5 mol) of $AgNO_3$. The mixture was homogenized for duration of 30 minutes and cast into films on clean microscope glass substrates. The samples were then dried at 50°C overnight prior to being irradiated with a UV light. For samples in colloid form, the mixture was irradiated consequently after being homogenized for 30 minutes.

The silver ions in the natural rubber matrix were reduced by means of UV irradiation. A high intensity UV light with a wavelength less than 300 nm was used. Samples were placed at a distance of 5 cm from the ultraviolet irradiation source.

2.2 Characterization

UV – Vis spectra of the NR – Ag films were recorded using a U – 2000 Hitachi UV Spectrophotometer within the wavelength range of 200 – 600 nm at room temperature. The absorbencies were determined as a function of time.

Transmission electron microscope (TEM), model JEM 1230 at 20kV was used to study the formation and average particle size of silver nanocrystals formed in – situ in rubber film and rubber latex. Preparation of the samples for TEM analysis differs in each case. Transmission electron microscope specimens were prepared by placing drops of the colloid mixture diluted five folds with distilled water onto carbon coated copper grids. The grids were then dried at 50°C prior to UV irradiation. The same procedure was used to prepare NR – Ag samples in latex form except the mixture was irradiated before being placed onto the grids.

Silver nanoparticle sizes were measured using a SIS – DOCU Image Analyzer. The mean particle diameter of 300 particles and standard deviation were calculated. Standard deviation was obtained via the following equation, $[n\sum x^2 - (\sum x)^2 / n (n - 1)]^{½}$ where n and x are the number of samples and average of total particles respectively.

The final products were also analyzed using X – ray diffraction. Characterization was carried out on a SIEMENS D5000 X – ray Diffractometer with a monochromatic Cu – Kα radiation filter in the 2θ range of 20 – 60°. Crystallinities of the silver nanostructures were assessed from their XRD patterns.

3. Results and Discussion

UV – Vis Spectra

The UV – vis absorption spectra were used to measure the formation of silver nanoparticles as a function of irradiation time. Figure 1 shows typical absorption spectra of silver nanoparticles formed in natural rubber films. The distinct absorption bands occur around 450 to 470 nm. These peaks are due to the surface plasmon resonance of the silver nanoparticles. The band shifts towards shorter wavelengths (blue shift) as irradiation time increases. This shows that the particle size becomes smaller with longer irradiation time[25]. The effect maybe explained by increasing electron density on the silver particles due to alteration of the Fermi level[22]. It has been reported that this blue shift is due to the formation of fluffy large particles at the initial stage of the reaction, which consists of smaller clusters. As the reaction proceeds, the larger particles will then fall apart giving rise to smaller particles[25 - 26].

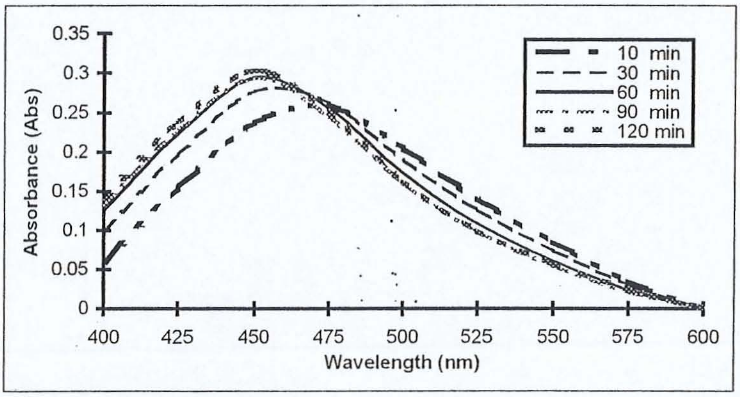
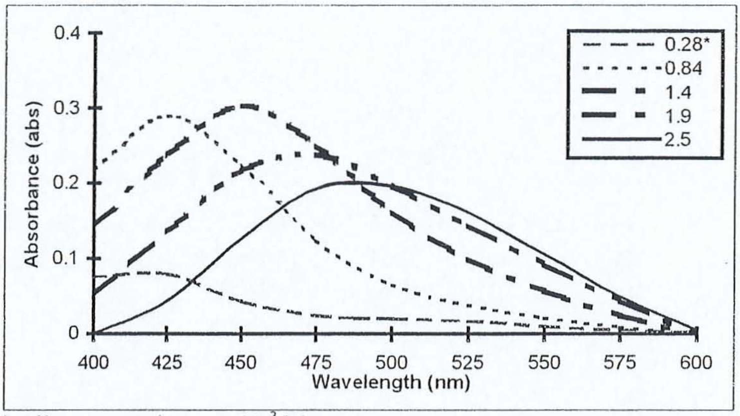


FIGURE I: Optical Absorption Spectra of Natural Rubber – Silver Film as a Function of Time.

Figure 2 shows the absorption spectra of silver nanoparticles formed in the natural rubber film synthesized using different concentrations of $AgNO_3$. The band shifts towards higher wavelengths (red shift) and broadens as the concentration increases indicating they have increasing average size of silver nanoparticles..



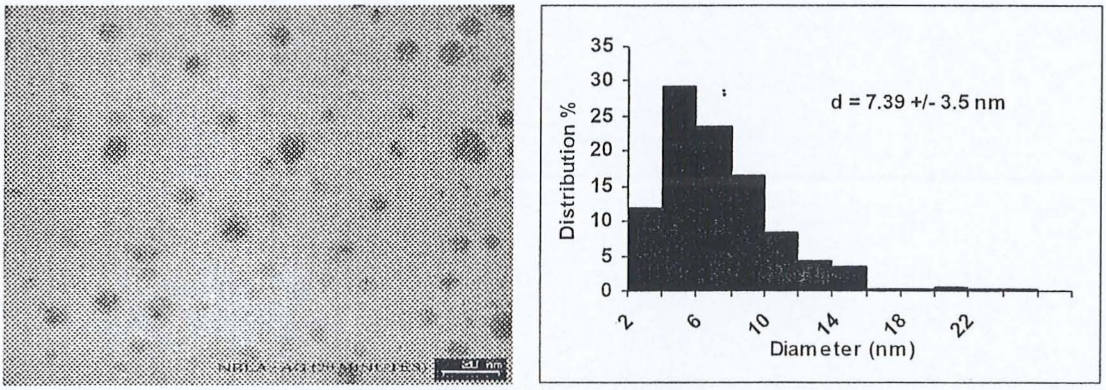
* All concentrations are 10^{-3} M

FIGURE II: Optical Absorption Spectra of Natural Rubber – Silver Film at Different Concentrations of $AgNO_3$.

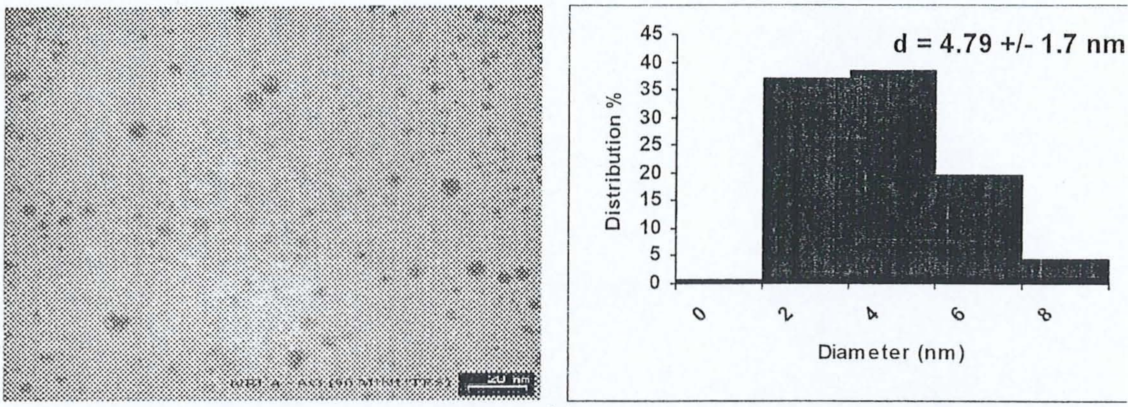
TEM Analysis

The average size of the silver nanoparticles was determined by TEM. Figure IIIa - b shows the electron micrograph and size distribution of silver nanoparticles in natural rubber film after 20 and 90 minutes of UV irradiation. All the silver nanoparticles are spherical with an average size of 7.4 +/- 3.5 nm after 20 minutes. With increasing irradiation time the average size of these silver nanoparticles decreases to a value of 4.79 ± 1.7 nm for 90 minutes of irradiation, as shown in Figure IIIb. These results are in accordance with that observed from the UV – vis absorption spectra.

When colloidal natural rubber latex containing silver nitrate was irradiated, different silver morphologies were obtained. Typical TEM images of a NR – Ag colloid sample are shown in Figure IIIa - b. A regular fractal nanostructure is observed. It is evident that a randomly ramified silver structure is present in the NR – Ag latex.



(a)



(b)

FIGURE III: TEM Image of Natural Rubber – Silver Film and Size Distribution of Silver Nanoparticles After (a) 20 Minutes and (b) 90 Minutes of UV Irradiation.

The growth phenomena of these fractals can be explained using models such as cluster – cluster aggregation (CCA) [27] and diffusion – limited aggregation (DLA) [28 - 29]. The fractal dimension (D) determines the model used. Here, we used the method reported by Forrest and Witten[30] to determine the D value. The TEM micrograph was digitized by hand using 'ones' and 'blanks'. The 'ones' correspond to the presence of particles whereas the blanks indicate the absence of particles. The number of particles (N) in squares of different sizes (l) was counted, and a graph log N vs log l was plotted (Figure IV). The fractal dimension, which is calculated from the slope, is 1.61. This value is in agreement with the D value for the DLA model, where $D \approx 1.67$ [29].

(a) (b)

FIGURE III: TEM Images of Natural Rubber – Silver Colloid After 90 Minutes of UV Irradiation.

Generally, the formation of fractals is caused by the non – equilibrium growth and molecular anisotropy[24]. In this case, based on the DLA model, the hitting and sticking process initiates the growth of fractals. Particles of different sizes, which bump into each other, through the random walk movement[9], have a tendency for the ions on the smaller particle to dissolve from its surface and precipitate onto the larger particles. This indirectly causes the larger particles to grow at the expense of the smaller particles[24].

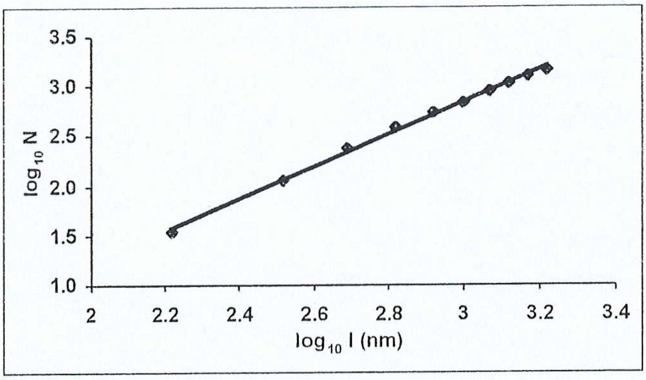
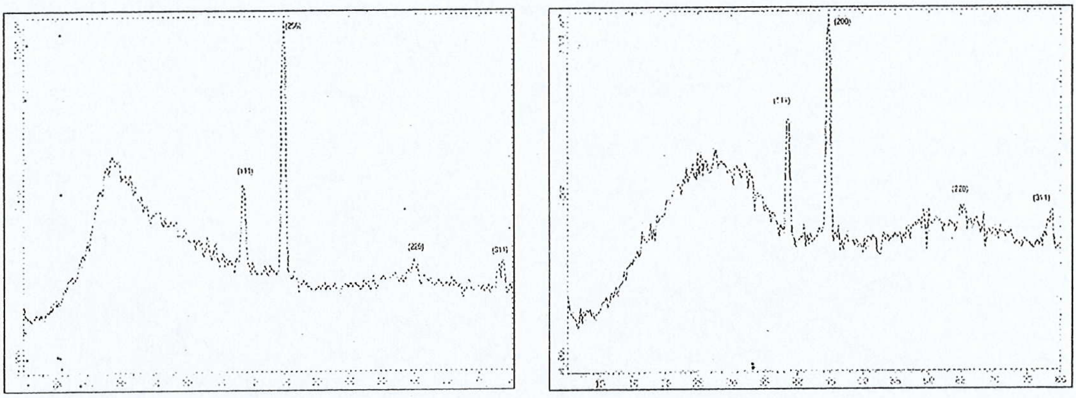


FIGURE IV: Plot of $Log_{10} N$ vs $Log_{10} l$ plot to determine the Fractal Pattern of Natural Rubber – Silver Colloid.

XRD Analysis

Finally, X – ray diffraction analysis was adopted to determine the products in the samples. The X – ray patterns show that only the Ag peaks were observed in both samples. The peaks are indexed to the (111); (200), (220) and (311) planes as shown in Figure Va - b. These peaks correspond to the face centered cubic (fcc) phase of Ag as reported before[7, 8, 23]. From the patterns obtained, the Ag in both samples has high crystallinity.



(a) (b)

FIGURE V: XRD Patterns for (a) Natural Rubber – Silver Film, (b) Natural Rubber – Silver Colloid.

4. Conclusion

In conclusion, a novel system was used to synthesize Ag nanostructures by means of UV irradiation. Natural rubber was used as a matrix both in the form of a film as well as colloid. We have shown that NR – Ag composite films prepared on glass substrates, produced dispersed silver nanoparticles with an average size of 4.79 ± 1.7 nm. UV – vis analysis proved that the size of these particles decreased with irradiation time. In contrast, when a colloid mixture of natural rubber and $AgNO_3$ was irradiated, fractal growth formation was observed. The value of the fractal dimension D = 1.61,

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