

Epoxidised Natural Rubber-Stabilised Gold Colloids Prepared in an Organic Mixture of Toluene and 2-propanol

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A direct synthesis of gold nanoparticles in a purely organic environment using 2-propanol as the reducing agent and epoxidised natural rubber (ENR-50) as the polymer stabiliser is described. Experimental parameters such as reaction temperature and concentration of gold ions were scrutinised in order to study the effect on size, morphology and dispersion of the gold nanoparticles. Preparations at temperatures $\leq 70^{\circ}\text{C}$ or employing high concentrations of gold ions produced large particles of various geometrical structures with some of sponge like appearance while those prepared at $\geq 80^{\circ}\text{C}$ or at low concentrations of gold ions produced fine particles of spherical or near spherical shape. The particles were well dispersed in the ENR matrix. The formation of ENR-stabilised gold organosol was relatively fast ca. 1–3 hrs. Therefore synthesis of ENR-gold composite in organic solvent was capable of producing small sized and spherical particles when the synthesis was carried out at high temperatures and low concentration of gold ions was used.

Key words: gold colloids; epoxidised natural rubber; nanoparticles; 2-propanol; organosol

The major challenge in colloidal metal preparation is the ability to control particle size, dispersion, stability and particle morphology. Reduction techniques, stabilisers and reaction conditions employed will largely determine the outcome of the colloid. Reducing methods such as chemical¹, electrochemical², electromagnetic³ and sonochemical⁴ have been widely used for the synthesis of colloidal metals. The chemical reducing agents commonly used are borohydride⁵, hydrazine⁶, sodium citrate⁷ and alcohols⁸. Most of the metal precursors and reducing agents are

water soluble. Different reducing agents exhibit different reducing abilities which influence the rates of reduction, and also determine the morphological outcome of the metal particles. One of the most investigated metals is gold. Colloidal gold has long been known for its therapeutic and curative properties to treat various ailments such as venereal diseases, dysentery, epilepsy and tumors⁹. Gold nanoparticles are currently being developed for applications in catalysis¹⁰, sensors¹¹, as well as electronic¹², superparamagnetic¹³ and drug delivery¹⁴ devices. This recent advancement is

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a result of the quantum size effect of the nanoparticles¹⁵. Apart from that, gold is chemically inert or stable and the nanosized gold particle is capable of various definite morphologies and shapes such as nanowire¹⁶, nanorod¹⁷, pseudo-trigonal, decahedral and sphere¹⁸ which give rise to different properties. Upon nucleation, the metal particles formed will often aggregate to larger particles¹⁹. To limit this, stabilisers such as ligands²⁰, surfactants²¹ and polymers²² are usually used. Most polymer stabilisers are synthetic polymers such as polyvinylpyrrolidone (PVP)²³, polyvinyl alcohol (PVA)²⁴, polyethylene glycol (PEG)²⁵ and polymethylmethacrylate (PMMA)²⁶. Few natural polymers have been employed as stabiliser for the synthesis of metal particles. Among them are starch⁹, chitosan²⁷, gelatin²⁸, cellulose²⁹ and tripsin³⁰. However, natural rubber and its derivatives have been least employed as stabiliser for the preparation of colloidal metals. Epoxidised natural rubber, ENR is a modified natural rubber with epoxide groups incorporated into the isoprene chain. It possesses improved properties which is comparable to some specialty elastomers³¹. Thus ENR has recently been formulated into polymer blends³², adhesives and electrolytes³³. ENR is a water insoluble polymer and dissolves in only a limited number of organic solvents such as toluene, chloroform and tetrahydrofuran. This limits synthetic protocols for ENR-metal composites. We have recently reported the preparation of ENR-Ag organosols which employ the technique that enables aqueous to the organic phase transfer³⁴. This technique provides a route for the preparation of metal particles in the organic phase. In this study, another approach of preparing colloidal metal in a purely organic environment is described. This is exemplified by a direct synthesis of gold organosol in the presence of epoxidised natural rubber (ENR-50) as stabiliser using 2-propanol as the

reducing agent. Although it has been reported that the synthesis of metal organosols often yielded large particles with uncontrollable morphology, this paper attempts to address the said issues *via* the study on the effect of reaction temperature and gold ions concentration in relation to the production of fine gold colloids.

EXPERIMENTAL

Materials

The following chemicals were obtained commercially and were used without further purification; hydrogen tetrachloroaurate trihydrate (auric acid), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma), 2-propanol (Merck), toluene (Fisher Chemicals). Epoxidised natural rubber with 50% epoxidation (ENR-50) was supplied by Guthrie Polymers (Malaysia) Sdn. Bhd.. The ENR-50 was purified according to Lee and co-workers³⁵.

The progress of metallic gold formations was monitored using a Hitachi U-2000 UV-vis spectrophotometer. The sample solutions were contained in a 10 mm quartz cuvette. The colloidal gold generated a characteristic surface plasmon resonance (SPR) that was detectable at 400-700 nm range. FT-infrared spectra were obtained using a Perkin-Elmer System 2000 infrared spectrometer. The samples were prepared by forming a thin film by drop casting the sample solution onto a ZnSe window. TEM samples were prepared by spreading two to three drops of the sample colloids onto a carbon coated 400 mesh copper grid followed by drying in air for at least one day. TEM micrographs were taken with a Philip CM12 transmission electron microscope (TEM) operating at 80kV. The size and size distribution of particles were obtained using an image analysis computer software "analySis

Docu” Version 3.2 (Soft Imaging System GmbH, Munster, Germany). Unless otherwise stated, these measurements were taken from at least 300 particles. The X-ray diffraction analyses of the composite thin films formed upon evaporation of the colloids on a glass substrate were performed using a SIEMENS D5000 X-ray powder diffractometer equipped with a monochromatic Cu-K α radiation filter in the 2 θ range of 0° – 100°.

Preparative Procedure

Preparation of stock solutions. Stoichiometric calculation was carried out by considering one repeating unit of ENR-50 as a component consisting of one unit of isoprene with one unit of epoxidised isoprene with the molecular formula of $-(C_{10}H_{16}O)_n-$. The molecular weight was 152.22 g mol $^{-1}$ when $n = 1$. Thus, 6.569×10^{-5} mol mL $^{-1}$ of ENR-50 was prepared by dissolving 500 mg of ENR-50 in 50 mL of toluene. For gold, 8.26×10^{-6} mol mL $^{-1}$ stock solution was prepared from 65 mg of auric acid dissolved in 10 mL of 2-propanol.

Preparation of ENR-50-gold organocolloids. The volume ratio of toluene to 2-propanol solution mixture was fixed at 4 to 1 with the overall total volume of reaction mixture for each experiment as 25 mL.

(a) *Effect of preparation temperature.* For all experiments, the reaction flask was immersed in a paraffin oil bath. The bath temperatures used were room temperature, RT (~30°C), $50 \pm 2^\circ\text{C}$, $70 \pm 2^\circ\text{C}$, $80 \pm 2^\circ\text{C}$ and $90 \pm 2^\circ\text{C}$ (reflux temperature). For the preparation of 1700:1 of ENR to gold ions ratio, 7.61 mL of ENR-toluene stock solution (5×10^{-4} mol mL $^{-1}$) was adjusted to 20 mL by adding 12.39 mL of toluene and stirred for 10 min in a round bottom flask. 0.08 mL of auric acid in 2-propanol stock solution (3.64×10^{-6} mol mL $^{-1}$) and 4.92 mL of 2-propanol were then

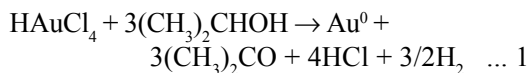
added while the mixture was vigorously stirred. The UV-vis absorption spectra of the reaction mixture was taken (at room temperature) after two minutes of stirring. The reaction mixture was then heated to and maintained at the desired temperature. The UV-vis absorption spectra of the reaction mixture that followed were taken at various time intervals.

(b) *Effect of gold ions concentration.* The experiment was conducted at molar ratios of ENR to gold ions of 1700:1, 1000:1, 500:1, 100:1 and 40:1. All experiments were performed at bath temperature of $80 \pm 2^\circ\text{C}$. Typical preparations and sampling for the UV-vis absorption spectra were as described in (a) above.

RESULTS AND DISCUSSION

Synthesis of ENR-gold Organocolloids

Gold particles were prepared from auric acid using 2-propanol as the reducing agent. Isopropanol is miscible in aqueous and toluene and thus functioned as a mediator between the aqueous-organic phases. The reduction of the auric acid using 2-propanol is according to Equation 1³⁶.



The reaction conditions of gold ions concentration, reaction duration and temperature were studied accordingly. It is well-known that the oxirane group of ENR easily undergoes ring opening reaction at low pH (< 3). To avoid ring opening, this study employs pH > 3 (*ca.* 4.8–5) in the various ENR to gold ions molar ratios used.

The formation of metallic gold particles in toluene/2-propanol mixture containing ENR-50 is confirmed by XRD analyses. A typical XRD

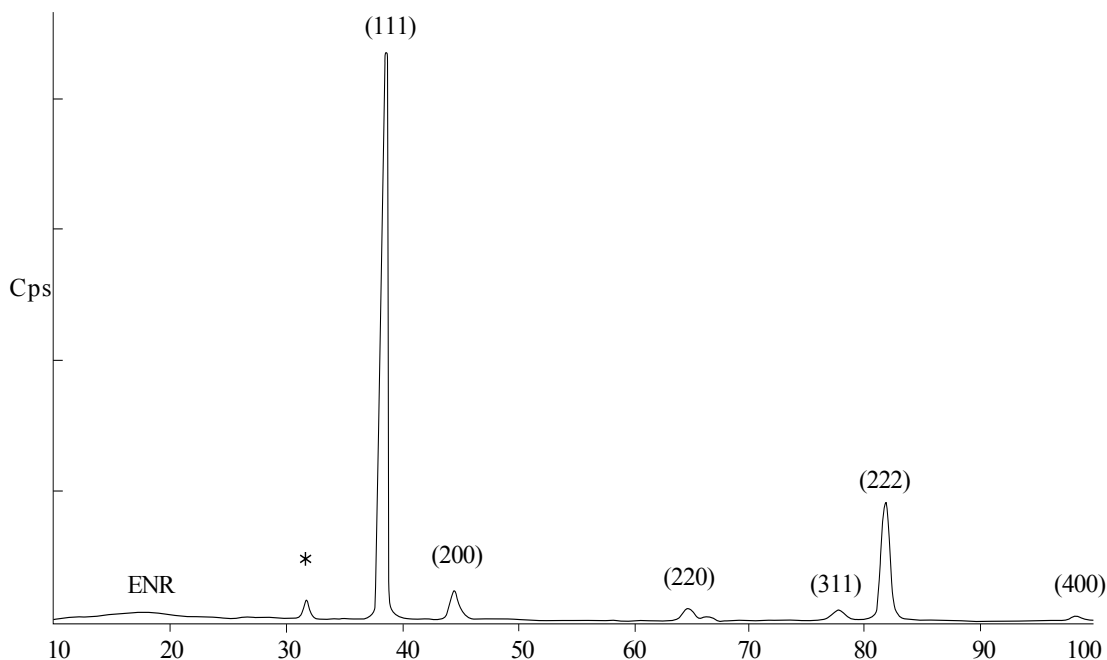
pattern of the prepared gold organocolloids is shown in *Figure 1*. The gold particles in ENR matrix exhibited diffraction peaks that correspond to the reflection planes of 111, 200, 220, 311, 222 and 400 at the respective 2θ angles of 38.2° , 44.4° , 64.6° , 77.6° , 98.1° and 110.1° . These reflections and the corresponding 2θ angles indicated a face-centered cubic (fcc) lattice of the metallic gold³⁷. The very broad peak at 2θ of $\sim 10^\circ - 25^\circ$ in the diffractogram was due to the amorphous nature of ENR (while the remaining peak marked with asterisk (*) was due to the impurity in the glass substrate used³⁸).

The FTIR spectra of all the prepared gold organocolloids within the described experimental conditions did not show any

significant shifts in frequency of the oxirane and the vinyl groups in ENR. Hence there was no definite chemical interaction between the ENR matrix and the gold particles.

Effect of Preparation Temperature

Samples with ENR to gold ions ratio of 1700:1 were prepared at various temperatures. As shown in *Figure 2a*, at 3 hours of reaction, the preparation at room temperature showed a UV-vis maximum absorbance (λ_{\max}) at 550 nm. This was followed by λ_{\max} 's at 540 nm, 530 nm and twice at 525 nm for respective temperatures of 50°C , 70°C , 80°C and 90°C . It could be seen that an increase in the preparation temperature resulted in a decline



*Figure 1. Typical XRD diffractogram of ENR-Au composite film (ENR to gold ion molar ratio of 40:1; * peak due to impurity originating from the glass substrate).*

in the value of λ_{\max} . It inferred to an increase in reduction reaction. The relationship of these λ_{\max} 's with reaction duration is depicted in Figure 3b. Preparation at 90°C showed the fastest reduction. This was followed in descending order of 80°C, 70°C, 50°C and room temperatures. It was noted that the UV-vis absorbance intensity for preparations at 80°C and 50°C were almost the same. The only difference between these temperature conditions was that the reduction at 80°C reached a maximum after the first hour of reaction while at 50°C, the maximum was reached only after three hours of reaction. The shorter time needed for the reductions to reach constant absorbance implied that the reduction of the gold ions was faster. The rate of reductions influenced the size of the

particles formed. Higher reduction rates often resulted in smaller particles³⁹. This was caused by the rapid exhaustion of the gold ions and upon nucleation the metallic gold particles formed would be stabilised by ENR that would prevent further growth and coalescence. Meanwhile, larger particles were formed with slower reduction at temperatures < 70°C.

Figure 3 shows the TEM micrographs, size and size distribution of the gold particles produced at various temperatures. At temperatures $\leq 70^\circ\text{C}$, there existed mixtures of trigonal, hexagonal, spherical and even rod-like particle morphologies. However, at temperatures $\geq 80^\circ\text{C}$, the particle was mainly of spherical shape. This confirmed that large particles absorbed at longer wavelengths while

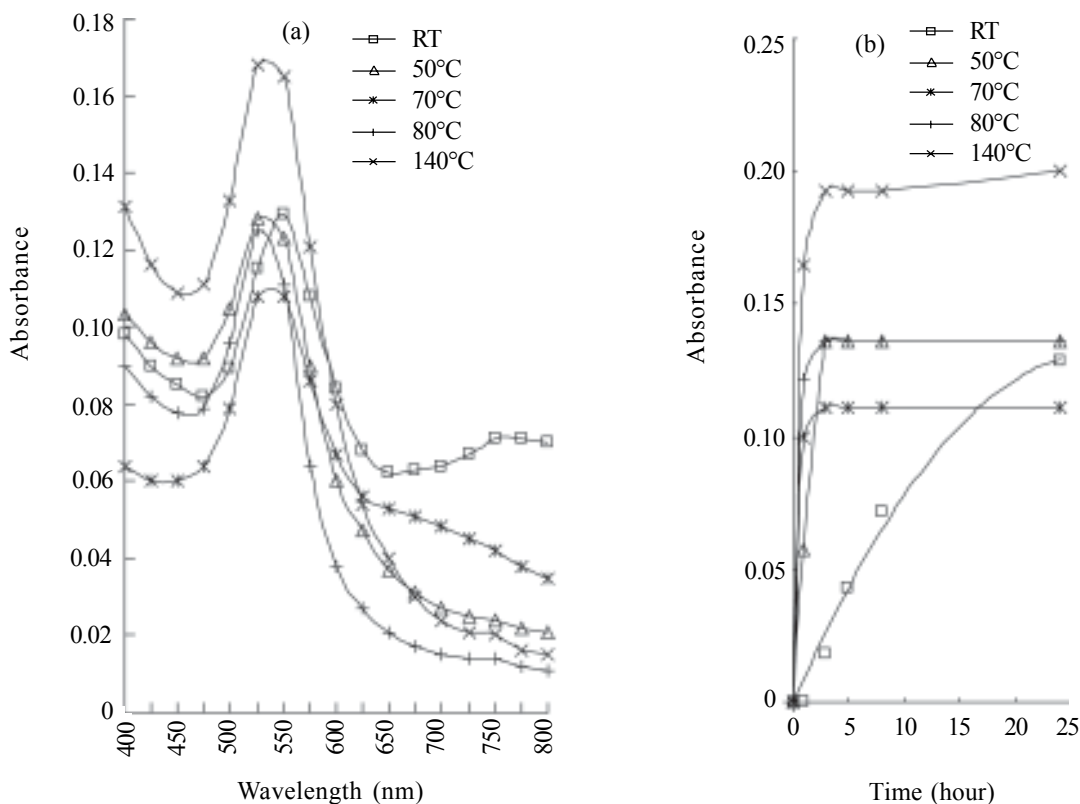


Figure 2. (a) UV-vis spectra of gold colloids at ENR to gold ions molar ratio of 1700:1 prepared at various temperatures at 3 hrs of reaction and (b) evolution of λ_{\max} w.r.t. time.

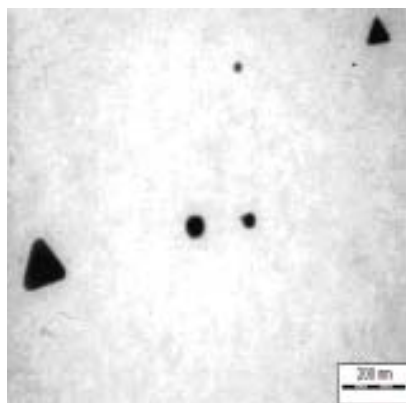
small particles, at shorter wavelengths of the UV-vis frequency range⁴⁰. There was a sharp decline in the average particle diameter when temperature was increased. At room temperature, the average particle diameter was 45.6 ± 19.1 nm. The average particle diameters obtained at 50°C, 70°C, 80°C and 90°C were 22.3 ± 11.9 , 16.6 ± 6.4 , 10.3 ± 5.1 and 9.6 ± 3.5 nm respectively. This showed that the reduction rate did influence the growth of the particles. As discussed earlier, the reactions at 80°C and 90°C showed similar λ_{max} of 525 nm but the latter exhibited a broader spectrum as shown in *Figure 2a*. This may be attributed to the smaller or different shaped particles produced for the preparation at a much higher temperature⁴¹.

Effect of Gold Ion Concentration

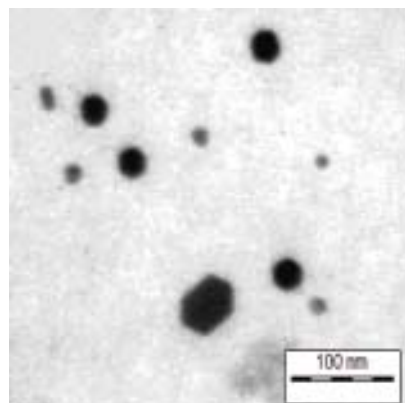
The effect of the various gold ion concentrations on the formation and characteristic of ENR-Au organocolloids at 80°C was investigated. At high concentrations of gold ions, *i.e.* the ENR to gold ions molar ratios of 40:1 and 100:1, the colour of the organocolloids were blue and brown respectively. For molar ratio of 500:1, the colloid was brown while at lower concentrations of gold ion (*i.e.* 1000:1 and 1700:1), the respective colours were purple and pink. The UV-vis absorbance at the ENR to gold ions molar ratios of 40:1 and 100:1 as depicted in *Figure 4a* were broad. These usually corresponded to larger particles and a wider size distribution. For the ENR to gold ions molar ratio of 500:1, a weaker and almost monotonous absorbance was observed. On the other hand, at the lower concentrations of gold ions, the absorbance profiles were narrower in shape. *Figure 4b* shows the reduction profiles of gold particles. At higher concentration of gold ions, the reduction was faster. Although it was reported that faster reduction affords smaller particle size⁴², it is

not observed in this case. The preparation with 40:1 molar ratio comprised of the largest particles among all the other ratios even though it indicated the highest of reduction, as shown in *Figure 5a* and *Figure 5b*, due to aggregation. The high concentration of gold ions yielded a high number of gold nuclei that later grow to form primary particles. The small amount of ENR-50 available was insufficient for the particle stabilisation and therefore lead to aggregation. In this case the particle-particle interaction was greater than the particle-polymer interaction. There were many distinctive geometrical shapes of gold particles formed at the ENR to gold ions molar ratios of 40:1 and 100:1. These geometrical shapes may have contributed to the broadness of the UV-vis absorbance. The 500:1 sample of ENR to gold ions molar ratio did not show any typical particle shape. The particles observed were also less in number as compared to the other preparations. As a consequence, the average particle size and size distribution were calculated based on less than 50 particles. These particles were fluffy and sponge-like adopting the form of truncated cubes *Figure 5c*. This was the main difference between these preparations. The existence of fewer particles with irregular shapes may have caused the flat and weak SPR absorbance as observed in *Figure 4a*. However, at lower concentration of gold ions, smaller and near spherical shape particles were observed as shown in *Figure 5d* to *Figure 5e*. This is consistent with the UV-vis spectra depicted in *Figure 4a* where the peaks are more distinctive.

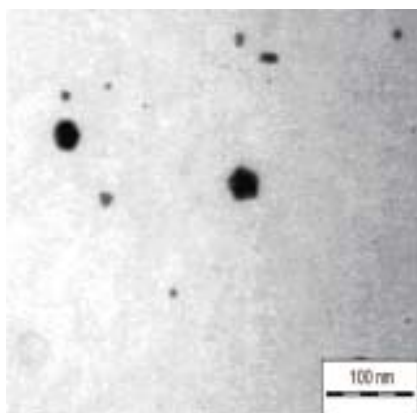
The blue (ENR to gold ions molar ratio of 40:1) and brown (100:1) gold colloids consisted of larger sized particles with an average diameter of 568.2 ± 206.2 nm and 500.3 ± 236.5 nm respectively. The 500:1 sample was also a brown colloid but had an average particle diameter of 145.0 ± 109.0 nm. The purple (1000:1) and pink (1700:1) colloids, yielded gold particles of 10.5 ± 4.7 nm and



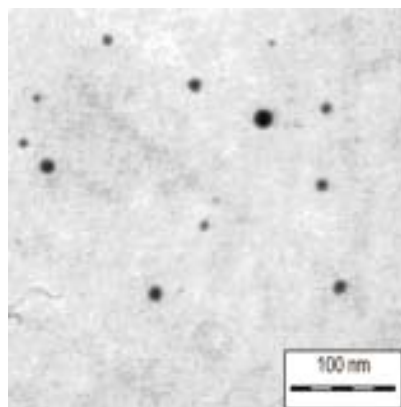
(a)



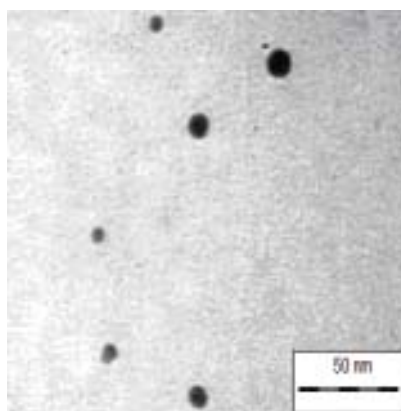
(b)



(c)



(d)



(e)

Figure 3. TEM micrographs of gold colloids at ENR to gold ions molar ratio of 1700:1 prepared at (a) RT, (b) 50°C, (c) 70°C, (d) 80°C and (e) 90°C.

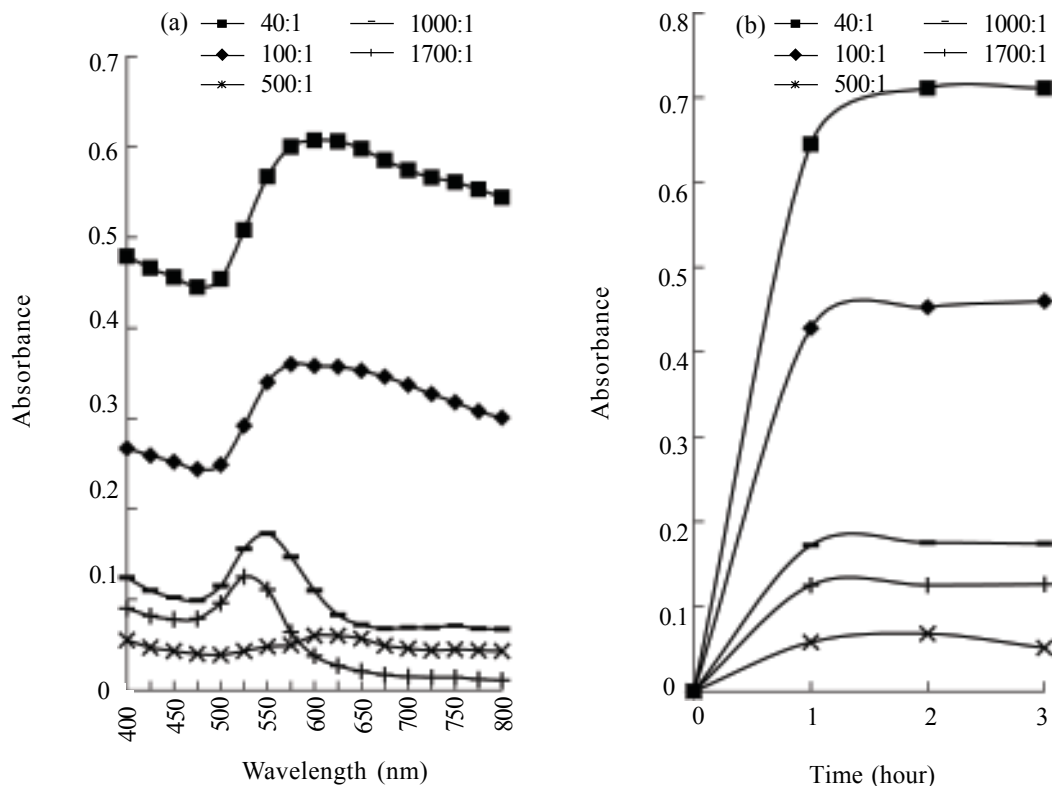


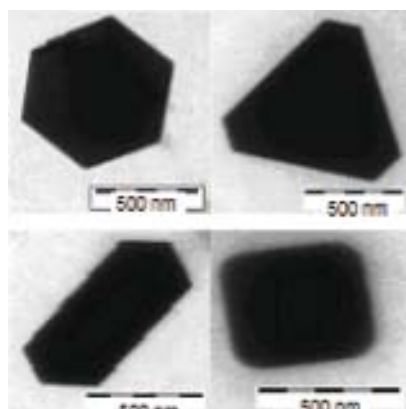
Figure 4. (a) UV-Vis absorbance spectra of gold colloids at various ENR to gold ion molar ratios (3 hrs reaction time) and (b) evolution of λ_{max} w.r.t. time (all reactions at 80°C).

9.6 \pm 3.5 nm average diameter respectively. Thus as the concentration of gold decreased, the size of the particles decreased and ENR behaved as a better stabiliser at low concentration of gold ions. It was previously reported that metal ions were trapped within the polymer chain before reduction⁴³. Generally, at high concentrations of gold ions (ENR to gold ions molar ratios of 40:1 and 100:1) the ions tended to accumulate within the ENR polymer chains. Therefore, upon reduction, the particles formed will inevitably aggregate before any stabilisation by the ENR chain can be effective. In contrast, at low concentrations of gold ions (i.e. 1000:1 and 1700:1), the ions were highly dispersed within the polymer chain and upon reduction the particles were efficiently stabilised within the

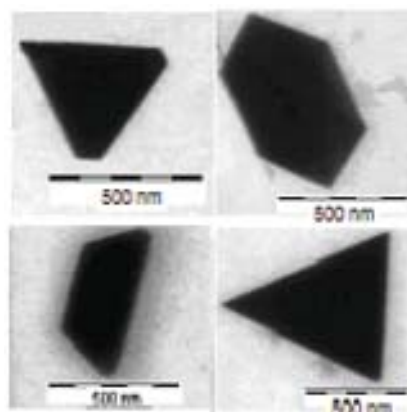
ENR chain. Therefore, the preparation with ENR to gold ions molar ratio of 500:1 can be pictured as the “turning point” for the formation of either large or small particles.

Morphological Transformations

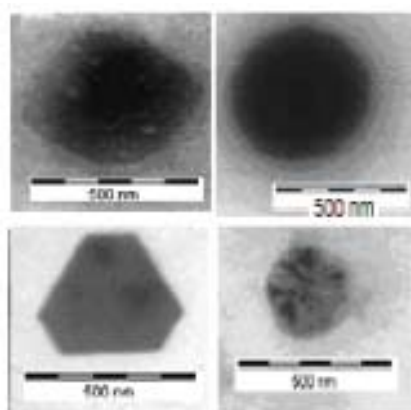
The recent interest in theoretical treatment⁴⁴ of particle morphological transformations has prompted us to include this section. Our previous report⁴⁵ on the ENR-gold organosols prepared at two different temperatures *via* the *in-situ* technique has shown that the size of the gold particles formed is dependent on the rate of gold ions reduction. Slower reduction rate produce large particles of various morphological shapes while faster reduction



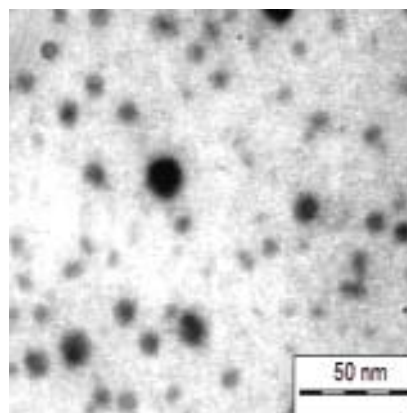
(a)



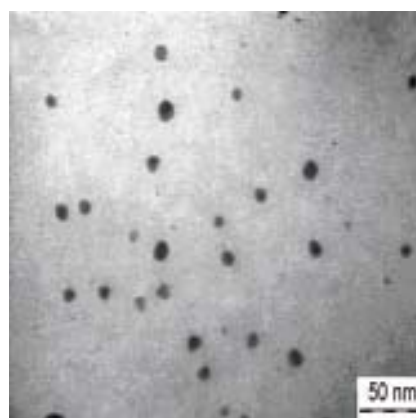
(b)



(c)



(d)



(e)

Figure 5. TEM micrographs of gold colloids prepared at various molar ratios of ENR to gold ion at 80°C (a) 1400:1, (b) 1000:1, (c) 500:1, (d) 100:1 and (e) 40:1.

tends to produce small and spherical particles. These morphologies observed are in accordance with some previously proposed mechanisms^{19,46-49}. These mechanisms assume orderly assembly of the primary particles that are formed upon nucleation. The final size and shape of the particles are therefore largely determined by the rate of nucleation that is dependent on the reaction temperature, strength of reducing agent and effective stabilisation. The present work has further confirmed that the preparation temperatures and the gold ion concentrations exert influence on the morphology of the as-formed particles. The morphological transformations of gold nanoparticles prepared at various gold ion concentrations and reduction temperatures are clearly observed. Thus the gold particles obtained at lower preparation temperatures ($\leq 70^{\circ}\text{C}$) are a mixture of crystalline particles with identifiable shapes. However, at higher preparation temperatures ($\geq 80^{\circ}\text{C}$), the gold particles are smaller in size and are mostly spherical or near spherical in shape. As discussed earlier, the formation of large crystals (ENR to gold ions molar ratios of 40:1 and 100:1), sponge-like particles (500:1) and spherical particles (*i.e.* 1000:1 and 1700:1) is basically affected by the concentration and the stabilising ability of the ENR matrix. The gold nanoparticles formed with ENR to gold ions molar ratio of 500:1 are mostly sponge-like or fluffy in nature. As explained by Chow and Zukoski⁵⁰, the sponge-like particles are comprised of loosely packed primary particles. This particles will break apart and consequently aggregate into various crystalline shapes as well as spheres. Thus depending on the amount of ENR presence, the higher ENR content stabilises the particles more effectively such that small and spherical particles are obtained. Otherwise large and variously shaped

crystals are obtained when low amounts of ENR is used. This is obvious as the low amounts of ENR and the consequent ineffectiveness to stabilise gold particles has allowed orderly arrangements of the particles to form large morphological structures.

CONCLUSION

ENR acted as a stabiliser for the synthesised gold organosols. At normal organosol pH (*ca.* 4.8–5), the FTIR analysis suggested that the presence of gold particles had least affected the structure of the ENR. Manipulation of gold ion concentrations and preparation temperatures had enabled control on the size and morphology of the gold particles in the synthesised ENR-gold composites. These experimental parameters influenced the reduction rate and the environment surrounding the nanoparticles that consequently influenced the formation of the gold nanoparticles. It was found that small particles were produced at low concentration of gold ions and high preparation temperature. Larger particles tended to show a variety of morphology with several identifiable geometries while smaller particles were usually spherical in shape. It is therefore possible to prepare ENR-gold composites with gold particles size to *ca.* > 10 nm and of spherical shape in a totally organic environment.

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