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Synthesis of Modified Natural Rubber-stabilised Silver Organosols via *Liquid-to-liquid Transfer Techniques*

M. ABU BAKAR*#, W.L. TAN*, N.J. AZIZI* AND N.H.H. ABU BAKAR*

A simple one- and two-step phase transfer technique in synthesizing silver nanoparticles is described. The silver ions are reduced using sodium borohydride either before (one-step method) or after (two-step method) adding the organic phase. 2-propanol was employed as a transferring agent whereas tetraoctylammonium-bromide and 50% epoxidised natural rubber (ENR-50) was used as the stabiliser in aqueous and organic layer, respectively. Both of the methods described are of comparable efficiency in transferring ions/particles whereby based on the atomic absorption spectroscopy determination, more than 93% of the silver ions/particles were transported into the toluene layer. The samples were characterised by UV-vis, FTIR, TEM and XRD. The UV-vis spectra and XRD pattern indicated the formation of silver nanoparticles. Size and size distribution analysis of the as-formed silver nanoparticles showed that two-step phase transfer method gave smaller particle size as well as narrower size distribution. The average size and standard deviation of silver nanoparticles for the one-step and two-step method in the organic layer was 18.4 nm ± 9.5 nm and 15 nm ± 5.8 nm, respectively.

Key words: silver; organosols; modified natural rubber; phase transfer; nanoparticles; tetraoctylammonium-bromide; ENR-50; AAS determination; FTIR; TEM; XRD; UV-vis

Nanomaterials have sparked much attention among scientists over the past decade. Due to their extremely small size they possess very different characteristics from their bulk materials[1,2]. Among these, silver nanoparticles have been extensively studied because of their potential applications in photographic science, catalysts, pigments, antimicrobials, optical and electronic devices and the like[3,4]. Hence, numerous methods such as microwave irradiation[4], UV-irradiation[5], reverse micro-emulsions[6] and chemical reduction[7] have been employed in synthesising finely dispersed silver nanoparticles.

Preparation of colloidal metals *via* liquid-to-liquid transfer is a renewed method that was first introduced by Faraday[8]. Basically, this technique involves transfer of ions or particles from an aqueous to an organic phase or vice versa. In general, two reagents are needed in this method *viz*. phase transfer agent and stabiliser[9]. The most common stabilisers used in the organic phase are mercaptopropionic

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acid[10], alkylamines[11], bis(ethylhexyl)hydrogen phosphate (HDEHP)[12], fatty amines[13] *etc*. Nonetheless, the usage of polymer especially natural polymers and their derivatives as stabilisers in an organic layer is scarcely reported.

NR is a natural polymer widely used in industrial manufacturing, such as tyres, gloves, hoses *etc*. However, it cannot compete with other synthetic elastomers in terms of gas permeability, oil resistance and certain mechanical properties[14]. Thus, various types of modified NR have been introduced. Among the chemical modifications, epoxidation is a simple and efficient method. Epoxidised natural rubber (ENR) exhibits low glass transition temperature, soft elastomer characteristics, high oil resistance and good elasticity[15]. Recently, it has been studied for use in polyelectrolyte by Razali and co-workers[16,17]. However, its potential as a stabilising agent or matrix for metal nanoparticles remains unexplored. Furthermore, ENR can only dissolve in limited organic solvents. In order to prepare ENR-stabilised metal organosols a liquid-to-liquid transfer is the preferred technique.

In this study, we report a simple one- and two-step liquid-to-liquid transfer technique in synthesizing silver nanoparticles employing ENR-50 as the stabilising agent/matrix in the organic phase and tetraoctylammonium bromide (TOAB) as the transfer agent.

EXPERIMENTAL

Materials

The following chemicals were used without further purification: silver nitrate (Johnson Matthey, U.K.), sodium borohydride (Riedel-de Haen), chloroform (Systerm, Malaysia), toluene (Fisher Scientific), 2-propanol (R&M Chemicals), n-hexane (Merck) and tetraoctylammoniumbromide 98%, TOAB (Aldrich Chemicals). Epoxidised natural rubber with 50% epoxidation (ENR-50) was kindly supplied by Guthrie Polymer (Malaysia) Sdn. Bhd. and was purified according to literature before used[18].

Preparation and Phase Transfer of Silver Colloids

Two-step method.

Silver colloids

Appropriately 0.27 mL of 3.734×10^{-6} mol mL^{-1} aqueous silver nitrate stock solution was pipetted into a bottle; 0.40 mL of neat TOAB and 4.73 mL of distilled water were added and the solution was stirred magnetically. A few drops of 1×10^{-5} mol mL^{-1} of chilled $NaBH_4$ solution was then added to the stirring solution as a reducing agent for the silver ions. The colour of the mixture changed progressively as the silver particles were formed.

Phase transfer

Appropriately 5 mL of 2.50×10^{-5} mol ml^{-1} ENR-50 in toluene stock solution and 5 mL of 2-propanol was added to the above mixture while vigorously stirring. After 2 min, the stirring was halted and the mixture was left to separate.

One-step method. Similar procedure as in the 'two-step method' (above) was employed for the 'one-step method', except the reducing agent $NaBH_4$ was added after the phase transfer. In a typical experiment, 0.27 mL of 3.734×10^{-6} mol mL^{-1} silver nitrate stock solution was pipetted into a bottle:

0.40 mL of neat TOAB and 4.73 mL of distilled water were added and stirred magnetically. Appropriately 5 mL of 2.5×10^{-5} mol mL^{-1} ENR-50 in toluene stock solution and 5 mL of 2-propanol was added to the above mixture while stirring. Finally, few drops of 1×10^{-5} mol mL^{-1} of chilled $NaBH_4$ were added dropwise into the mixture. After 2 min, the stirring was halted and the mixture was left for separation.

Characterisation

The optical properties of silver nanoparticles (both in the aqueous and organic phase) were measured using HITACHI U2000 UV-vis spectrophotometer. The sample solution was placed in a quartz cuvette and scanned within the range of 200 nm to 600 nm. The FTIR spectrum was recorded using the Thermo Nicolet IR200 spectrometer. The samples were dropped and cast to form a thin film onto a ZnSe window. The FTIR spectrum was collected in the region from 4000 cm^{-1} to 650 cm^{-1}. Powder X-ray diffraction (XRD) was used to characterise the samples in the form of thin film. The samples were prepared by casting the silver colloids onto a clean and dried microscope glass slide. Data were collected on a SIEMENS D5000 X-ray diffractometer with monochromatic Cu Kα radiation filter in the 2 θ range of 0º to 100º. The size and morphology of the silver nanoparticles were obtained using a Philip CM 12 transmission electron microscope (TEM) operating at 80 kV. The TEM samples were prepared as follows: a drop of colloidal solution was carefully placed on a carbon film coated copper grid and the solvent was evaporated off. The particles' diameter was measured using a computer program 'analysis Docu 2.11' (GmbH Germany). Average particle size and size distribution were obtained from ~300 particles. The standard deviation of the particle size was calculated using the following equation:

$$\sigma^2 = \frac{\Sigma(x_i - x)^2}{N} \quad \ldots 1$$

The residual silver content of the aqueous phase samples was determined using atomic absorption spectroscopy (AAS). As much as 1 mL of dispersion was taken from the aqueous part of the sample and digested with aqua-regia before AAS measurements.

RESULTS AND DISCUSSIONS

Synthesis

Before reduction of silver nitrate with sodium borohydride, the solutions were pale yellow in colour. When the silver salt was stirred with isopropanol and ENR-toluene, a milky white emulsion formed. As sodium borohydride solution was added dropwise to the emulsion, the colour of the emulsion progressively changed to milky brown. When the stirring was halted, the mixture gradually separated into two phases where the upper organic layer consisted of silver nanoparticles which adopted a dark brown appearance and the bottom aqueous layer became colourless as shown in *Figure 1a*.

For the two-step method, the silver colloids were pre-formed in the aqueous phase by the typical borohydride reduction as shown below (*Equation 2*):

$$2AgNO_3 + 2NaBH_4 + 6H_2O \rightarrow 2Ag^0 + 7H_2 + 2H_3BO_3 + 2NaNO_3 \quad \ldots 2$$

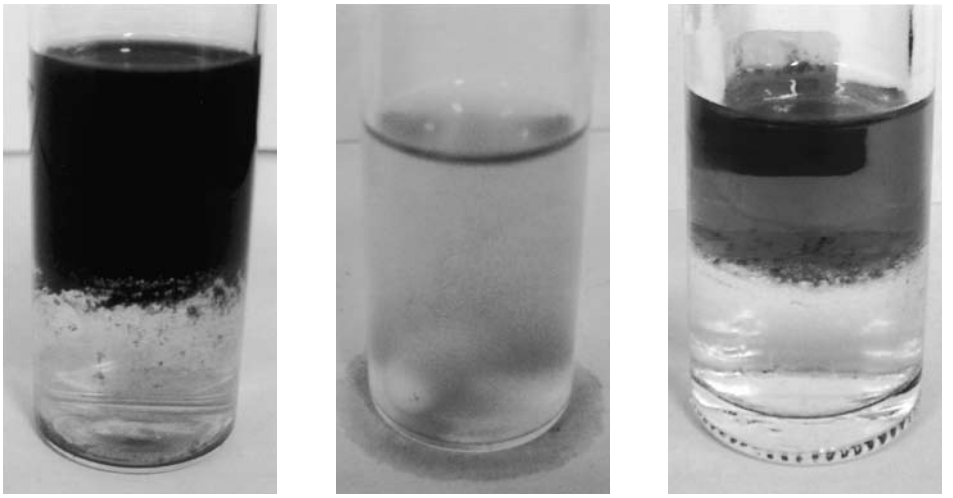
The formation of silver nanoparticles can be observed through the colour changes[5], where it shifted from colourless to yellow as depicted in *Figure 1b(i)*. Isopropanol and ENR-toluene were then added as transferring agent and polymer-organic solvent respectively, while vigorously stirring. Upon standing, phase separation took place. The bottom aqueous layer slowly became colourless while the silver

particles transported into the organic layer gave rise to an orange brown colour [*Figure 1b(ii)*]. A slight variation was evident in the colour of the phases before and after phase transfer which may be due to the changes in the overall particle sizes and the phase medium.

The progress of silver ion reduction was monitored using UV-Vis spectrophotometry. The optical properties of the silver nano particles using one- and two-step phase transfer method is shown in *Figure 2*. Both methods showed typical silver nanoparticle absorbance in the range of 350 nm to 500 nm. The absorption bands corresponded to the surface plasmon resonance (SPR) of silver nanoparticles caused by the oscillation of the conduction electrons[19]. The absorption band for silver organosols using one-step phase transfer was very broad. It showed a maximum absorption peak (λ_{max}) at 465 nm. The broadness of the absorption band is usually inferred as due to the existence of a broad particle size. On the other hand, the UV-Vis spectra for the two-step method both before and after phase transfer gave a narrower peak with the λ_{max} at shorter wavelengths as compared to the one-step method. The silver hydrosol in the two-step method showed a λ_{max} at 412 nm. The position of this peak was red-shifted to 420 nm for silver organosol. Furthermore, the width of the resonance band was found to broaden too. It is widely accepted that the broadening and shifting of the plasmon band is associated with the agglomeration of particles[20]. This is further confirmed by the TEM analysis. Both methods were found to be quite efficient in transferring silver particles based on AAS results. However, the two-step method gave better particle transfer efficiency where 97.6% of the silver particles were transported into the ENR-toluene phase as compared to the one-step method that offered only 93.8% efficiency.

Characterisation

TOAB is a known phase transferring agent besides being a stabiliser[21]. From the FTIR



a *b(i)* *b(ii)*

Figure 1. Photograph of (a) one-step and (b) two-step method: (i) before and (ii) after transfer.

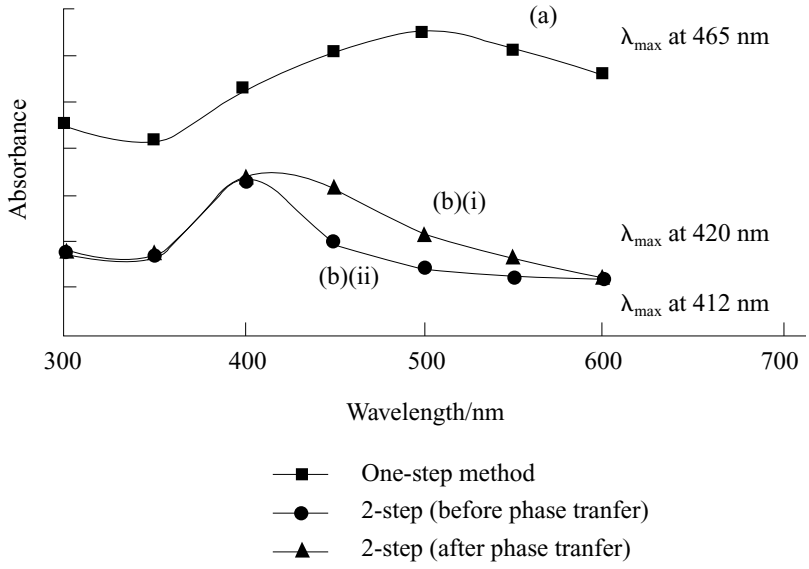


Figure 2. UV-Vis spectra for (a) one-step and (b) two-step method: (i) after (organosol) and (ii) before (hydrosol) transfer.

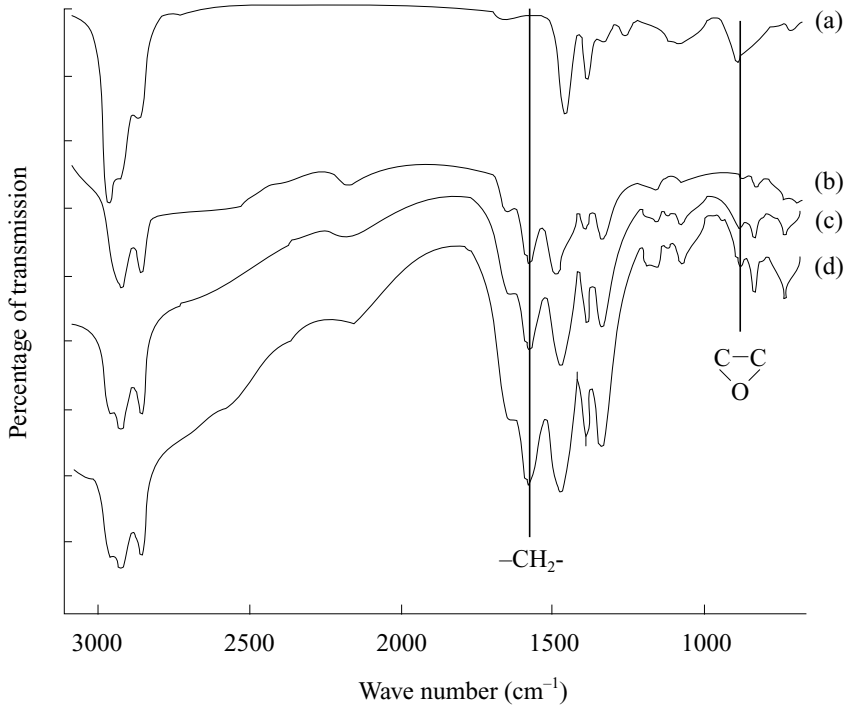


Figure 3. FTIR spectra of (a) neat ENR-50; (b) TOAB, (c) one-step method (organic phase) and (d) two-step method (organic phase).

spectra in *Figure 3*, both TOAB and ENR were present in the organic layer. This was confirmed by the presence of absorption peaks at ~2922 cm^{-1} and ~2853 cm^{-1} that were due to the respective anti-symmetric and symmetric $–CH_2-$ stretching vibrations of the carbon chains (overlapping by both ENR-50 and TOAB); the absorption bands at ~1567 cm^{-1} and ~1465 cm^{-1} arises from the $–CH_2-$ bending of the TOAB tail and the characteristic feature of epoxide ring of the ENR was situated at ~876 cm^{-1} (Pavia *et al*.[22]).

The XRD analysis was conducted to determine the phase of the sample in the organic layer. From *Figure 4*, the typical diffraction peaks from the samples indicated that the crystalline silver particles exhibited the face center cubic phase. The diffraction peaks at 2 θ of 38.1º, 49.9º, 64.5º and 77.2º correspond to the Miller indices for the reflection planes of (111), (200), (220) and (311), respectively[23]. Thus the silver ions were successfully reduced to silver metal. The broad peak at 2 θ of ~8º–18º was attributed to the halo-ENR.

Morphology

Most of the observed silver particles were in near spherical shapes and were independent of the methods used. However, the silver particles appeared to be bigger in size when one-step phase transfer method was employed. The formation of these bigger particles can be explained by two possible mechanisms as discussed by Duff and co-workers[24]. They were the autocatalytic reduction of metal ions on the as-formed particles surface or the coalescence and combination of clusters.

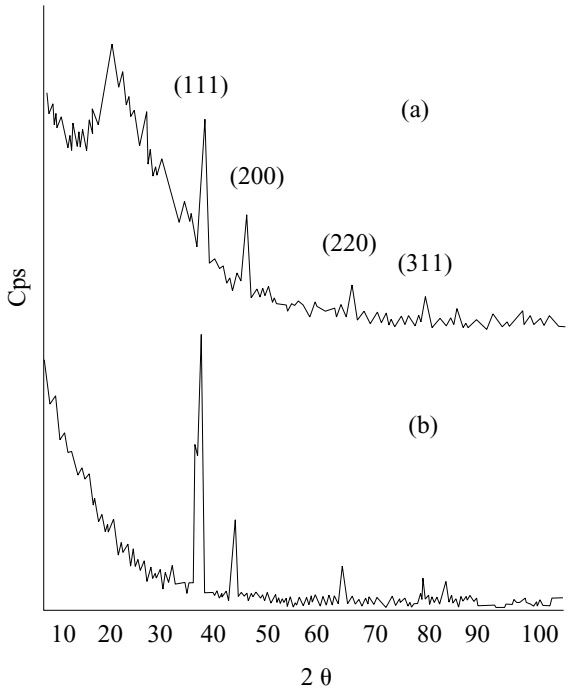


Figure 4. Typical XRD diffractogram of the sample prepared by (a) one-step method and (b) two-step method (organic phase).

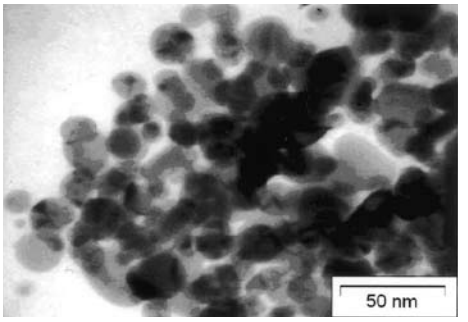
The particles were also highly agglomerated as depicted in *Figures 5a(i-ii)* which was reflected by the broad resonance plasmon band in the previously discussed UV-Vis spectra. It gave larger average sizes with a wider size distribution as compared to the two-step method (*ca*.18.4 nm and standard deviation of ± 9.5 nm). This could be explained by the steric hindrance caused by both the ENR and TOAB during the formation of silver nanoparticles. The 'crowding' of stabilisers (*viz*. TOAB and ENR) in the mixture will lead to the destabilisation and therefore the occurrence of aggregations and or agglomerations. To further confirm this explanation, a one-step phase transfer experiment without the use of TOAB was carried out. It was found that the silver nanoparticles were smaller in size and well dispersed in ENR-toluene phase, *Figures 5 b(i-ii)*. This thus confirmed that in the former, TOAB and ENR did intermingle and caused a lesser stabilising effect on the particles that led the particles to agglomerate. In the absence of TOAB, the ENR chains freely acted as stabiliser for the particles.

The average size and standard deviation of the silver nanoparticles before and after phase transfer for the two-step method was 14.5 nm ± 5.3 nm and 15 nm ± 5.8 nm, respectively. The average size as well as standard deviation of silver particles after phase transfer gave a slight increment which may be due to the small amount of multiparticle aggregates. The dispersity of the silver particles was more dispersed in the aqueous phase (*i.e.* before phase transfer) with the TOAB as stabiliser *Figures 5c(i-ii)*. When the silver particles migrated into ENR-toluene phase, they tend to agglomerate as shown in TEM micrographs [*Figures 5d(i-ii)*]. TOAB also migrated to the organic phase as shown by the results from the FTIR and XRD. When phase transfer took place, some of the TOAB migrated into the organic phase together with silver nanoparticles. TOAB will compete with the silver nanoparticles in terms of space and therefore most of the silver particles agglomerated well.

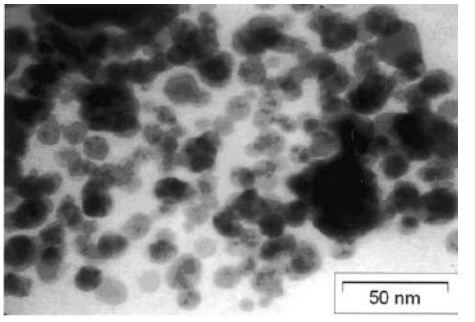
Mechanism of Transfer

As shown in *Figure 7*, the mechanism of two-step transfer is proposed as follows: the TOAB adsorbed on the surface of the silver nanoparticles *via* the head group and the hydrophobic tail is directed away from the center of the particles thus acting as protective agents in the aqueous phase preventing the close contact of the particles. Under vigorous stirring, the silver nanoparticles were extracted into the ENR-toluene phase with the aid of 2-propanol. The TOAB stabiliser also acted as a transferring agent. Some of the TOAB stabilisers together with silver nanoparticles migrated into the toluene layer, while the excess TOAB remained in the aqueous phase. In the toluene layer, the silver nanoparticles were either trapped within the voids of the ENR chain or stabilised by the TOAB *via* the head group and the latter similarly trapped in the ENR inter-chain network.

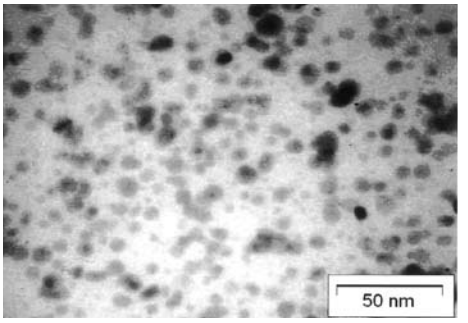
For the one-step synthesis, the mechanism of formation and transfer for silver nanoparticles differed slightly to that of the two-step synthesis. As all the chemical components were mixed together in the biphasic medium, TOAB stabilised micelles were formed. Some of the ENR were enclosed in the micelles and or formed complexes with the TOAB. In this case, the polymer-TOAB interaction dominated and caused a significant lack of effective stabilisers in protecting the silver nanoparticles. The weak polymer-nanometal interactions and strong interactions between nanometal-nanometal resulted in aggregation of the silver particles. They would coalesce with the neighboring particles to form larger particles during the stirring. Upon standing, silver nanoparticles were transported into the toluene phase assisted by 2-propanol



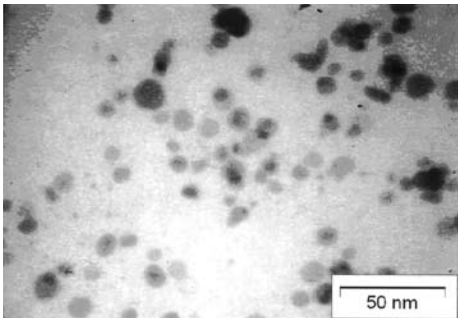
a(i)



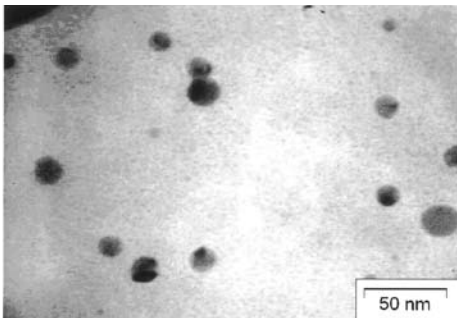
a(ii)



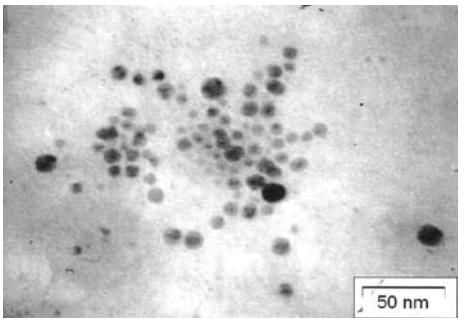
b(i)



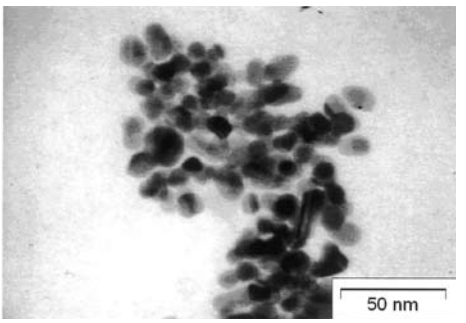
b(ii)



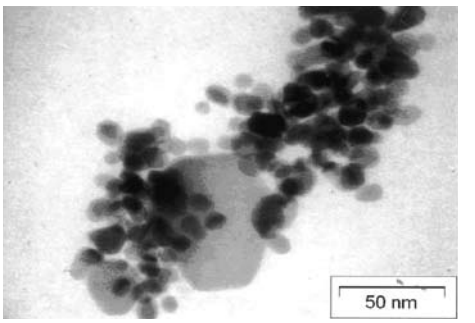
c(i)



c(ii)

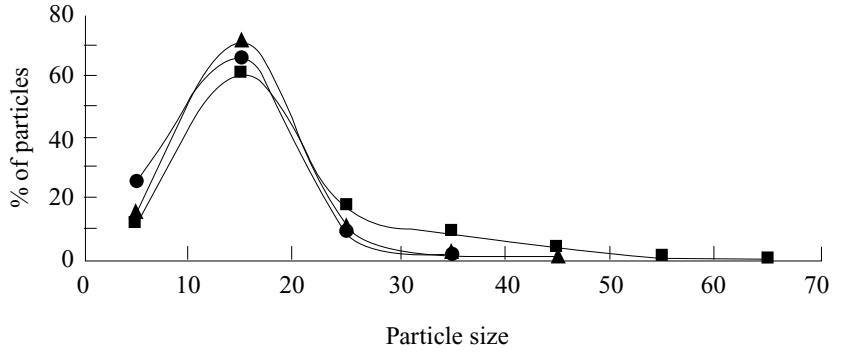


d(i)



d(ii)

Figure 5. TEM micrographs of silver nanoparticles: a(i–ii) organosol phase of one-step method and c(i–ii) hydrosol phase of two-step method and d(i–ii) organosol phase of two-step method and b(i-ii) one-step method without using TOAB.



Legend	Transfer method	Average size (nm)	SD
—■—	One-step method	18.4	± 9.5
—●—	Two-step (before phase tranfer)	14.5	± 5.3
—▲—	Two-step (after phase tranfer)	15.0	± 5.8

Figure 6. Size distribution, average size and standard deviation of silver nanoparticle synthesis by one-step and two-step phase transfer.

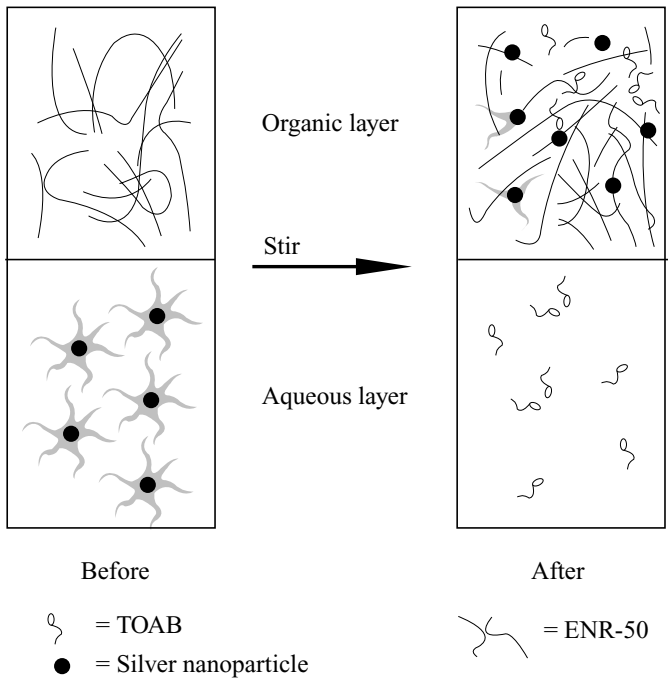


Figure 7. Proposed mechanism for two-step aqueous to toluene phase transfer of TOAB/ENR-stabilised silver particles.

as well as some TOAB. When TOAB was excluded in one-step synthesis, silver nanoparticles were trapped within the voids of the ENR and were weakly co-ordinated to the ENR chains. This would govern the size of the as-formed silver particles as the particles were enclosed in the inter-chain voids of the ENR.

CONCLUSION

ENR-stabilised silver organosol had been successfully synthesized *via* one-step and two-step liquid-to-liquid transfer techniques. Both methods gave comparable efficiency in transferring silver nanoparticles into the toluene layer. TEM analyses showed that the two-step transfer method gave smaller particles as well as a narrower size distribution as compared to the one-step method. The average size and standard deviation of particles after phase transfer slightly increased due to the steric hindrance caused by the existence of both ENR-50 and TOAB in the organic phase.

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