Research Article

Modified Natural Rubber Induced Aqueous to Toluene Phase Transfer of Gold and Platinum Colloids

Mohamad Abu Bakar, Jamil Ismail, Cheng Hoon Teoh, Wei Leng Tan, and Noor Hana Hanif Abu Bakar

Nanoscience Research Laboratory, School of Chemical Sciences, University of Sains Malaysia, Penang 11800, Malaysia

Correspondence should be addressed to Mohamad Abu Bakar, bmohamad@usm.my

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Citrate-stabilized gold and platinum particles were prepared in aqueous phase and transferred to toluene phase by employing 2-propanol as the transfer agent. It was found that the modified natural rubber (ENR) induced the phase transfer and assisted the dispersion of the citrate-free metal particles into the organic phase. The amounts of gold and platinum transferred are 93.4% and 86.1%, respectively. This phase transfer technique produced organosols of smaller particle sizes and narrower size distribution with self-assembly arrangements when compared to those prepared via the previous in situ preparations. The respective average particle size and standard deviation of gold before and after phase transfer were 6.3 ± 1.7 nm and 7.2 ± 1.3 nm, while for platinum they were 4.0 ± 0.7 nm and 4.2 ± 0.8 nm. The slight increase in the average sizes and overall size distributions in both metals after transfer was attributed to multiparticle aggregation in the organic phase.

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1. INTRODUCTION

Methods for the preparation of nanosized noble metals have been widely explored due to their importance in various applications [1]. Among the applications are sensors [2], catalysts [3], labels [4], as well as optical [5] and electronic materials [6]. In order to meet the requirements of these applications, particle synthesis has been tailored to meet specific features such as dispersity, size, and shapes [7]. These properties are dependent on the preparation environment and techniques. There are various routes to synthesize metal particles. Reduction methods such as chemical [8], sonochemical [9], electromagnetic [10], and electrochemical [11] have been reported. Chemical reduction is the most favored as a “bottom-up” approach.

It is well known that metal particles can be easily formed in aqueous compared to organic phase due to the ease of solubility of most metal precursors, chemical reducing agents (e.g., borohydrides and citrates), and stabilizers in water. This has afforded a wide range of metal hydrosols with various particle sizes and morphology as compared to metal sols prepared in the organic environment. To diversify the range of metal organosols, phase transfer of metal particles from aqueous to organic phase was introduced. In general, phase transfer technique has many advantages due to a number of factors. Among them is the ease of particles in the organic phase to adopt the size, size distribution and morphology of the particles prepared in aqueous phase. In addition, the particle size and morphology can be better manipulated due to the hydrosols that are already well formed prior to the particles transfer to the organic phase. The interaction between the metals and the organic solvents with or without stabilizer often creates particles self-assembly and this is advantageous in certain applications. Furthermore, aqueous to organic phase method enables the use of nonwater soluble stabilizers/matrix.

Transfer agents and particle stabilizers are often needed for such particle phase transfer processes. Among the transfer agents commonly used are tetrabutylammonium bromide (TOAB) [12], dimethyldioctadecylammonium chloride (DDAC) [13], concentrated hydrochloric acid [14], and alcohols (e.g., ethanol and 2-propanol) [15]. The common particle stabilizers are alkylamines (e.g., octadecylamine and dodecylamine) [16], alkythiols (1-dodecanethiol) [17], citrates, and surfactants (e.g., mercaptopropionic acid) [18]. A few of these stabilizers are also known to act as transfer
agents [16, 17]. Few polymers have been employed as stabilizers for particles in the organic phase. Esumi et al. employed a synthetic poly (amidoamine) dendrimer to encapsulate gold particles in an organic phase [19]. There are also few reports on the usage of natural polymers as stabilizers in a similar phase transfer process. We have previously reported the use of modified natural rubber (ENR-50) as the stabilizing agent or matrix for the silver nanoparticles in the organic phase [20]. Our work uses surfactant, tetraoctylammoniumbromide (TOAB), as the transferring agent. However, a trace presence of TOAB in the organic phase was observed. Therefore, the matrix comprising a mixture of stabilizer (TAOB) and polymer (ENR) encapsulates the metal particles. This can affect the properties of the resultant composite especially in certain applications such as in electrical conductive adhesive (ECA), thermal interface material (TIM), and polyelectrolyte. For the said applications, bare metal-polymer composites are much desired. The use of citrate as aqueous phase particle stabilizer is of particular interest as compared to alkylamines and alkylthiols. Unlike the latter, citrate has been reported to be completely detached or replaced by other organic soluble stabilizers upon particle transfer into the organic phase [16–18]. Thus, in this study, we report the use of ENR-50 that induces the aqueous to toluene transfer of citrate-stabilized gold and platinum particles and the ability of the ENR-50 to exert good dispersion of the citrate-free particles in the toluene layer.

2. EXPERIMENTAL

2.1. Materials

Hydrogen tetrachloraurate trihydrate, HAuCl₄·3H₂O and platinic chloride, H₂PtCl₆ (both from Sigma, USA), sodium borohydride, NaBH₄ (Riedel-de Haen, Germany), trisodium citrate, Na₃C₆H₅O₄·2H₂O (Ajax Chemicals, Australia), toluene (Fisher Chemicals, UK), and 2-propanol (Merck, Germany) were obtained commercially and used without further purification. Modified natural rubber with 50% epoxidation (ENR-50) was supplied by Guthrie Polymer Sdn. Bhd (Malaysia) and purified according to the previous report [21]. The average molecular weight of the purified ENR-50 is 400 000.

2.2. Preparation and phase transfer of metal colloids

2.2.1. Metal colloids

For the preparation of 20 mL aqueous gold colloids, 1.56 mL 2.54 × 10⁻⁵ mol mL⁻¹ of aqueous HAuCl₄·3H₂O stock solution was pipetted into a reaction flask and 18.04 mL of distilled water was added. The solution mixture was stirred with magnetic stirrer. A 0.4 mL of 3.0 × 10⁻³ mol mL⁻¹ trisodium citrate solution was then added and stirring was continued for a further 10 minutes. Subsequently, 0.4 mL of 1.0 × 10⁻⁴ mol mL⁻¹ of freshly prepared, chilled NaBH₄ solution was added.

Similarly, for the preparation of 20 mL aqueous platinum colloids, 1.44 mL of 2.74 × 10⁻⁶ mol mL⁻¹ aqueous H₂PtCl₆ stock solution and 18.16 mL of distilled water was mixed and stirred. A 0.4 mL of 3.0 × 10⁻⁵ mol mL⁻¹ solution of trisodium citrate was then added and stirred for another 10 minutes. This was followed by the addition of 2.5 mL of 1.0 × 10⁻⁴ mol mL⁻¹ of chilled NaBH₄ solution.

2.2.2. Phase transfer

A 5 mL of the respective metal colloids prepared above was added into a flask containing 5 mL of 2-propanol followed by vigorous stirring. A 5 mL of 2.50 × 10⁻² mol mL⁻¹ of ENR-toluene stock solution was then added. The stirring was stopped after 1 minute and the mixture was left standing for phase separation.

The role of 2-propanol and ENR in the phase transfer process was also investigated. Thus, experiments without the 2-propanol as phase transfer agent and another in the absence of ENR in the organic phase were similarly carried out as above.

2.3. Characterizations

Prior to any form of characterization, the organic layer of each preparation was separated and evaporated off. After that, 5 mL of toluene was added to redisperse the metal colloids and these were subsequently used for various characterizations as described below.

The size and morphology of the metal particles before (aqueous phase) and after (organic phase) phase transfer was analyzed using a Philip CM12 transmission electron microscope (TEM) operating at 80 kV. 5 drops of the respective metal colloids were cast onto a carbon coated copper grids and left to dry. The average size of the particles, standard deviations (SD), and size distributions were evaluated using the computer software “Analysis Docu 2.11” (Soft Imaging System GmbH, Munster, Germany). The optical property of the metal colloid was measured using a Hitachi U-2000 UV-vis spectrophotometer. The metal colloid was placed in a 1cm quartz cuvette and measured within the range of 200–800 nm. X-ray diffraction analysis was performed using a Siemens D5000 X-ray diffractometer with a monochromatic Cu-Kα radiation filter in the 2θ range of 0–100°. Samples were prepared as a thin film on a glass slide. The metal contents of the organic phase after phase transfer were determined using the Perkin Elmer 3100 flame atomic absorption spectrometer (AAS). The average molecular weight of purified ENR was determined using a Perkin Elmer 250 gas permeation chromatography (GPC). The structure of ENR was analyzed using Perkin Elmer System 2000 FT-infrared spectrometer.

3. RESULTS AND DISCUSSION

3.1. Synthesis

Aqueous solutions of chlorauric acid and chloroplatatinic acid in the presence of trisodium citrate were yellow and pale
When the respective citrate-stabilized metal hydrosol was stirred in the presence of ENR-toluene solution and 2-propanol, a milky emulsion was formed. The emulsion for gold was milky pink while that of platinum was milky white as shown in Plates 1(a)(ii) and 1(b)(ii), respectively. After phase separation, the bottom aqueous layer becomes colorless while the top organic layer adopts the color of the respective metal hydrosols, (Plates 1(a)(iii) and 1(b)(iii)). However, when 2-propanol was excluded from the preparation, no apparent transfer of the particles between the phases was observed, as indicated by the color of the respective phases. They retained their original colors. There was no exchange of particles between the phases although contact between the aqueous and organic interface was intentionally increased by stirring. Therefore, the particles phase transfer was assisted by 2-propanol which acted as the transfer agent. 2-propanol has a mutual solubility in aqueous and toluene solvents. Alcohol is known to act both as solvent and reducing agent for noble metals. However, the latter is only possible at elevated temperatures. The work described uses 2-propanol solely as the phase transfer agent that acts as the intermediary for both phases thus enabling the transfer of the metal particles between phases.
For these metal organosols, there are no significant changes observed from the FTIR spectra of ENR before and after phase transfer. A typical IR spectrum of the metal-ENR organosol is presented in Figure 2. The peaks due to the oxirane at 877 cm\(^{-1}\) [24] and the C=C at 840 cm\(^{-1}\) remained unchanged. Therefore, it is anticipated that there are no structural changes of the ENR chain. There was also no FTIR band attributable to the citrate observed in the organic phase, which meant that citrate was not transferred into the toluene phase. This implied that citrate stabilizers remained in the aqueous phase (probably due to the insolubility of citrate in toluene) after the transfer process of the respective metal particles to the organic phase.

The optical properties of the gold sols before (hydrosol) and after (organosol) phase transfer are shown in Figure 3. The citrate-stabilized gold hydrosol showed a typical absorbance at \(\lambda_{\text{max}}\) 525 nm that corresponds to the surface plasmon resonance (SPR) of gold nanoparticles [25]. After phase transfer, the \(\lambda_{\text{max}}\) is slightly red shifted to 530 nm. This red shift often indicated the formation of bigger particles but in this work, it may also be due to the variation in the solvent's refractive index on going from aqueous to toluene [16]. Other possible factors that may have caused this red shift are the changes in the adsorbed molecules on the particle surface (i.e., citrate stabilized to ENR stabilized) or the aggregation of the particles during the transfer process as previously reported [15]. Platinum sols do not exhibit SPR within the UV-Vis range studied.

The organic layers after phase transfer were subjected to the atomic absorption spectrophotometry (AAS). The AAS analyses of the organic aliquots showed that the average metal contents in the organic phase after the transfer of the metal particles are 93.4% and 86.1% for gold and platinum, respectively.

In order to ascertain the role of ENR as the stabilizer, an experiment was carried out using only citrate-stabilized metal hydrosols that were transferred into toluene without ENR. It was found that the particles tend to aggregate forming several masses of particles at the interphase as shown in Plate 4. This observation indirectly proved that the transportation of citrate into the organic phase did not occur. This is due to the low solubility of citrate in the toluene. Thus, without any stabilizer in the organic phase, the metal particles could not disperse well and therefore tend to agglomerate. Therefore, in those experiments where the ENR is included in the organic phase, the ENR is responsible for dispersing and stabilizing the transferred metal particles in the organosols. The ability of ENR to act as a stabilizer arises from its molecular structure and its chain conformation when in toluene solution. The degree of epoxidation, distribution of the epoxide group in the polymer chain, molecular weight and interaction between the chain and toluene molecules determined the chain conformation. In the case of ENR-50, an isoprene polymer with 50% mol epoxidation level and the average molecular weight of 400,000, the polymer chain resumes an extended coil conformation. This conformation is capable of accommodating the metal particles, brought to proximity by the carrier 2-propanol, and results in the metal particles entrapment in the coiled chains. This mode of particle stabilization is generally termed as trapped within the voids of the polymer chains [20]. Thus, the particle aggregations are inhibited. Therefore, in the presence of ENR, the ENR induces the transfer of metal particles (into the organic phase), assists in the particle dispersion by providing sites (voids) for the particle, and stabilizes the particles (within the voids) in the organosols. Although it has been reported that metal particles can interact with epoxide and the C=C groups of the ENR to form metal-complexes [26, 27], there is no evidence of such interactions or complexations was observed from the FTIR spectra as mentioned earlier.

3.2. Phase and morphology of gold and platinum particles

The ENR-gold organosol cast into film exhibited diffraction peaks at \(2\theta\) of 38.2\(^\circ\), 44.4\(^\circ\), 64.6\(^\circ\), and 77.6\(^\circ\) that corresponded to the lattice planes of [111], [200], [220], and [311], respectively, Figure 5(a). Similarly, the ENR-platinum film also exhibited the diffraction peaks corresponding to the lattice planes of [111], [200], [220], and [311] at the respective \(2\theta\) of 39.7\(^\circ\), 46.2\(^\circ\), 67.4\(^\circ\), and 81.2\(^\circ\), Figure 5(b). These lattice planes corresponded to the face-centered cubic (fcc) lattice of metallic gold and platinum, respectively [28, 29]. The very broad peak at \(2\theta\) range of \(\sim 10–30\(^\circ\)\) in both diffractograms was due to the halo-ENR.

The TEM micrographs and histograms for gold and platinum particles before and after phase transfer are depicted in Figure 6. The gold and platinum particles were self-assembled. The shapes of the particles in the aqueous phase are similar as those described by Yang et al. [15] using citrate as the stabilizer. The shape is basically retained upon the transfer to the organic phase. However, the platinum particles are less defined as compared to gold probably due to its smaller size. The average sizes and standard deviations of the gold particles before and after phase transfer are 6.3 ± 1.7 nm and 7.2 ± 1.3 nm, respectively. For platinum particles, however, the respective average sizes and standard deviations before and after phase transfer are 4.0 ± 0.7 nm and 4.2 ± 0.8 nm.
Generally, there is a slight increase in particle size and size distribution after phase transfer. For gold, the majority of the particles are situated around 6-7 nm range before the phase transfer. However, the amount of particles in the size range of 7-8 nm increased after phase transfer. Similarly, for platinum, the increase is from around 3-4 nm to 5-6 nm size range. Especially for gold, the increases in particle sizes and size distributions are in accordance with the red shift of the $\lambda_{\text{max}}$ as observed in the UV-Vis analysis. Generally, the increase in particle size may be due to the slight aggregation of the particles upon transfer from the aqueous to the organic phase [15]. As the particles move into the organic phase, they may come in contact with each other and aggregate due to the absence of citrate surrounding the particles before the particles are finally surrounded by ENR and hence inhibiting further growth.

### 3.3. Mechanism of interphase particles transfer

In the various phase transfer experiments, it was found that very little transfer of particles was observed without stirring. Similarly, without 2-propanol there is also no apparent particle transfer observed, even after prolonged stirring. In the absence of ENR, the metal particles tend to aggregate and accumulate at the aqueous/toluene interphase. For those successful phase transfer processes, no citrate was detected in the organic phase. This inferred that the metal particles underwent an exchange of stabilizers upon phase transfer, that is, from citrate stabilized in aqueous phase to ENR stabilized in the toluene phase. Therefore, addition of 2-propanol is required for phase transfer to occur with 2-propanol acting as the transfer agent while ENR acts as replacement stabilizer and therefore exerts dispersion of the particles in the toluene phase. It must be noted that in the several mechanisms previously reported, the stabilizers are often transferred along with the metal particles from the aqueous to organic phase, that is, without undergoing any exchange of stabilizers [30–33].

In this work, the probable mechanism of phase transfer is proposed as follows. Upon formation of the metal particles, they are initially stabilized by the citrate in the aqueous phase. The microemulsion was formed when hydrosol and ENR toluene in the presence of 2-propanol were mixed. The formation of the microemulsion increases the surface area between the organic and aqueous phase. The addition of 2-propanol will cause the transfer of the citrate-stabilized particles into the toluene layer due to the mutual solubility of alcohol in both solvents. Upon particle transfer, the particles undergo replacement of stabilizer from the citrate to ENR. This is facilitated by the structure of ENR-50 that is naturally loose and contains many interchain voids [34]. The citrate disentangled from the surface of the metal particles and remained in the aqueous layer as it is insoluble in toluene as previously evidenced by the FTIR results. Therefore, the presence of the ENR in the organic phase induces dispersion of the metal particles. The metal particles diffused into the voids and formed stable ENR-metal organosols as discussed earlier.

### 4. Conclusion

Citrate-stabilized gold and platinum particles had been prepared in aqueous phase via sodium borohydride reduction of their respective salts and subsequently transferred to the organic phase using 2-propanol as the transfer agent. An absence of ENR in the organic layer caused the metal particles to accumulate and form aggregates at the interphase. The presence of ENR in the organic phase induced the metal particles dispersity with only a minimal growth of the metals particles after phase transfer. Therefore, ENR can be used as a matrix and/or stabilizer for the transfer of citrate-stabilized gold and platinum hydrosol to the organosol. The dried metal colloids can be redispersed using various
Figure 4: TEM micrographs, average size, standard deviation (SD), and size distribution of ENR-stabilized gold nanoparticles at (a) before and (b) after phase transfer (scale bar = 50 nm) and platinum nanoparticles at (c) before and (d) after phase transfer (scale bar = 20 nm).
organic solvents that are compatible to ENR such as chloroform, tetrahydrofuran (THF), and the likes.

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