Reuse of Surfactant/Oil Phase in Nanoparticle Synthesis Using W/O Microemulsions

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Introduction

Preparation and application of nanosized materials are of significant scientific and industrial interests.[1–3] Currently many research groups are working in this area. A technique that has been developed over the past two decades involves the use of reverse micelles or water in oil microemulsions of surfactants as "nanoreactors".[4–8] The nanometer sized aqueous cores of the reverse micelles provide an appropriate stabilized environment for the production of nanoparticles of fairly uniform size, through the necessary chemical reactions within the core. In addition, the surfactant layer acts as steric stabilizer to inhibit the aggregation of nanoparticles formed, and keep it dispersed.

A large variety of nanoparticles have been prepared ever since the invention of the technique by Boutonnet et al.[9] A comprehensive account of this water-in-oil microemulsion technique can be obtained in reviews by Eastoe and Warne[10] and Pileni.[11]

Some advantages of using the microemulsion for nano particle synthesis are given below:

(a) At room-temperature and pressure, nanoparticles of a large number of materials can be prepared.

(b) This technique does not require any special equipment.

(c) It is possible to control the size and morphology of the particles formed.

(d) It can be utilized for carrying out all the precipitation reactions that are known, to obtain particles in homogeneous solution.

Although there are several advantages of producing nanoparticles by microemulsion technique, one of the constraining factors for large-scale production of nanoparticles by this method is the cost of the surfactant and oil phase, which constitute over 90% of total cost of production as the amount of nanoparticles produced is very small compared to the amount of surfactant/oil phase used.

The objective of this work is to develop a method to separate the nanoparticles from the surfactant/oil phase, and reuse the surfactant/oil phase to produce different batches of nanoparticles, and characterize and compare the characteristics of nanoparticles synthesized with reused surfactant and organic phase. For this study, we have chosen silver nanoparticles synthesized in water in oil microemulsions of AOT in heptane.

Materials and Method

AOT(sodium bis (2-ethyl hexyl)sulfosuccinate) was obtained from Sigma Chemicals. The n- heptane (>99%) used was refluxed over sodium for 3-4 h, and then distilled, to remove traces of moisture. The AR grade silver nitrate and the sodium borohydride were obtained from S.D. Fine Chem., India. The water used for preparing the electrolyte solution was doubly distilled.

Preparation of Nanoparticles

The water -in-oil microemulsions were prepared by mixing the aqueous solutions of silver nitrate (0.1 M) or reducing agent sodium borohydride (0.05 M) to 0.1 M AOT/heptane solution. 0.45 mL of 0.1 M silver nitrate solution was solubilized in 25 mL of 0.1 M AOT/heptane. A second microemulsion was prepared by solubilizing 0.45 mL of 0.05 M sodium borohydride in 25 mL of 0.1 M AOT/heptane solution. The molar concentration of silver nitrate and sodium borohydride were 1.8×10^{-3} and 9×10^{-4} mol dm^{-3}, respectively. The microemulsion containing sodium borohydride was added at once to the microemulsion containing silver nitrate. The

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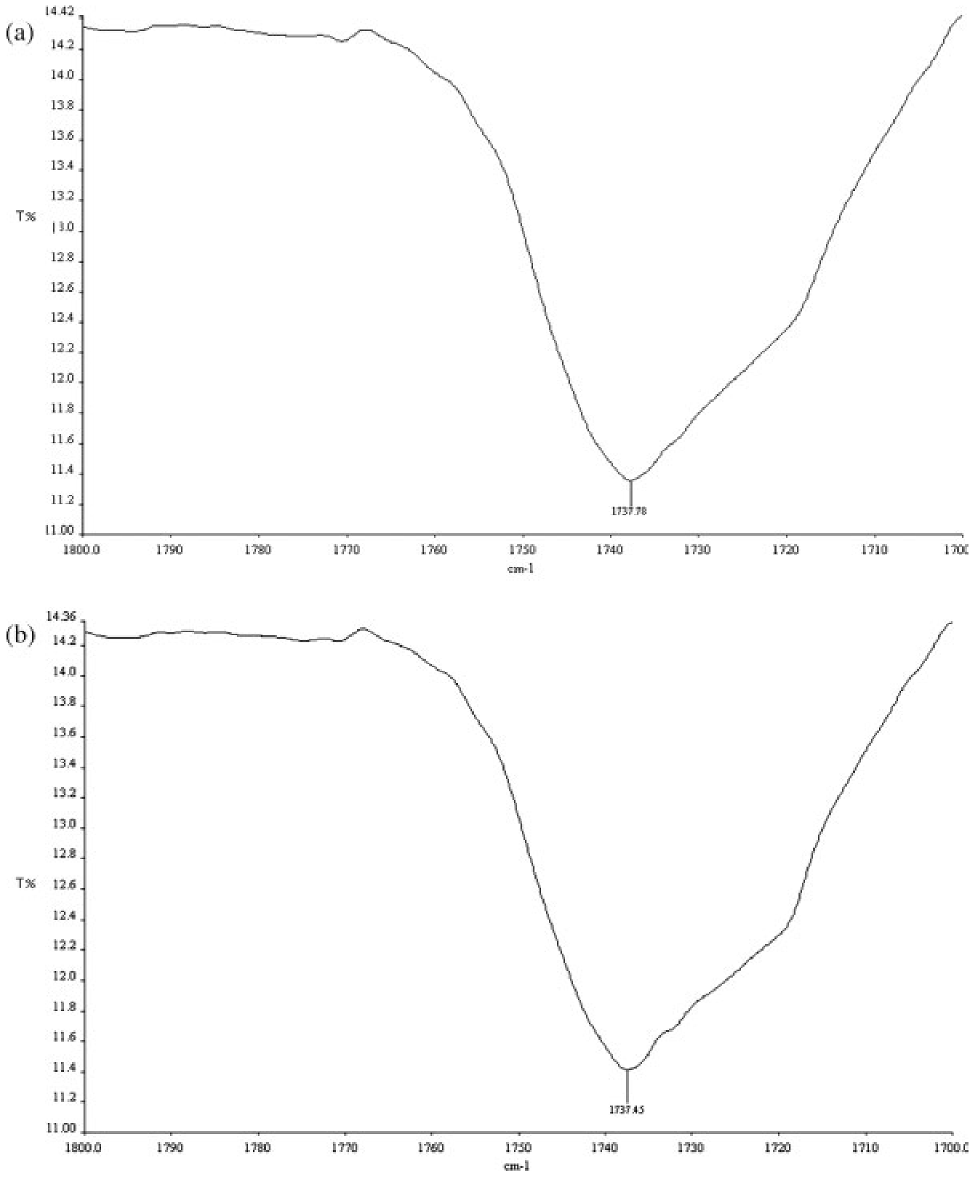

Figure 1. (a) FTIR spectra for AOT/heptane/water system; (b) FTIR spectra for filtrate.

mixture was shaken for half an hour to produce a third microemulsion containing silver nanoparticles. The water to surfactant molar ratio (R) was held constant at 10.

Spectroscopy studies

The absorption spectra were recorded using Shimadzu UV-visible spectrophotometer (UV 165). The reverse micelles containing nanoparticles were used directly for absorption studies. Same standard blank reverse micelle without reactants was used as a reference in UV-vis spectrophotometer.

Electron microscopy studies

A Philips CM200-TEM has been used to characterize the particle size and morphology. The maximum resolution of the instrument is 0.2 nm. TEM samples were prepared by placing a drop of microemulsion containing nanoparticles directly onto carbon coated copper grids. After 10 min the grids were dipped in sufficient amount of n-heptane, in order to remove all the surfactants and then dried for an hour under IR lamp before taking images.

Separation of nanoparticles

The nanoparticles were separated by ultracentrifugation. The ultracentrifuge used was Optima Max-E Ultracentrifuge (Beckman Coulter) (600 watts). The centrifuge was used at a "g" value of 50,000, which corresponds to 31,250 rpm. The centrifugation was carried out for total time of 1 h. The silver particles settled at the bottom of the centrifuge tube leaving behind a clear solution (filtrate 1). This solution consisted of oil phase, surfactant and water. The total electrical energy spent in separation was 0.6 Kilowatt-hour, and the operating cost of separation by ultracentrifuge (electricity cost) was

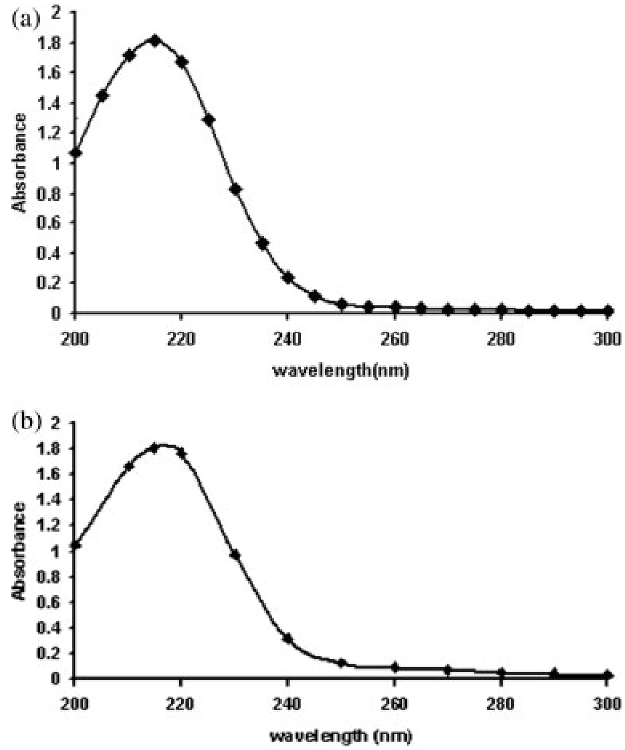

Figure 2. (a) UV-visible spectra of AOT/heptane/water system; (b) UV-visible spectra of filtrate.

less than 1% of the total cost of nanoparticle synthesis by this method.

Surfactant for reuse

Figures 1a and b show the FTIR spectra for AOT/heptane/water system (R = 10, [AOT] = 0.1 mol dm^{-3}), and the filtrate1, respectively. The peak at 1737 cm^{-1} corresponds to the carbonyl stretching peak of AOT/water/heptane system.[12] The positions (1737 cm^{-1}), as well as the intensity of the peaks are same in both cases.

Figures 2a and b show the UV-visible spectra of the initial 0.1 M AOT/heptane/water system and filtrate 1, respectively, against heptane/water as blank. Both spectra show the same peak at 215nm. The FTIR and UV visible studies, thus, indicate that there is no appreciable change in the concentration and structure of the surfactant in the filtrate.

The concentration of water in filtrate 1 was determined by automatic Karl Fisher titrator from Labindia. It was found that out of the 0.9 mL of water added to 50 mL of AOT solution, 0.89 mL of water remained in the filtrate 1. 0.01 mL of water was added to the filtrate to maintain a constant R value of 10.

Filtrate 1 was tested for presence of silver nitrate and sodium borohydride. To one part (5 mL) of the filtrate 1, silver nitrate solution (0.1 mol dm^{-3}) was added, and to the second part of the filtrate 1 (5 mL) sodium borohydride solution

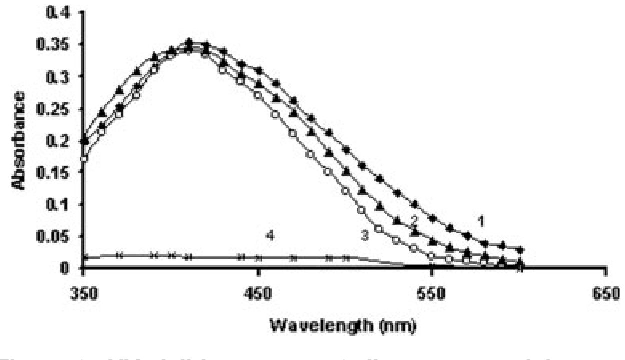

Figure 3. UV-visible spectra of silver nanoparticles.

(1) Initial AOT/heptane/water system; (2) first reuse; (3) second reuse, and (4) filtrate.

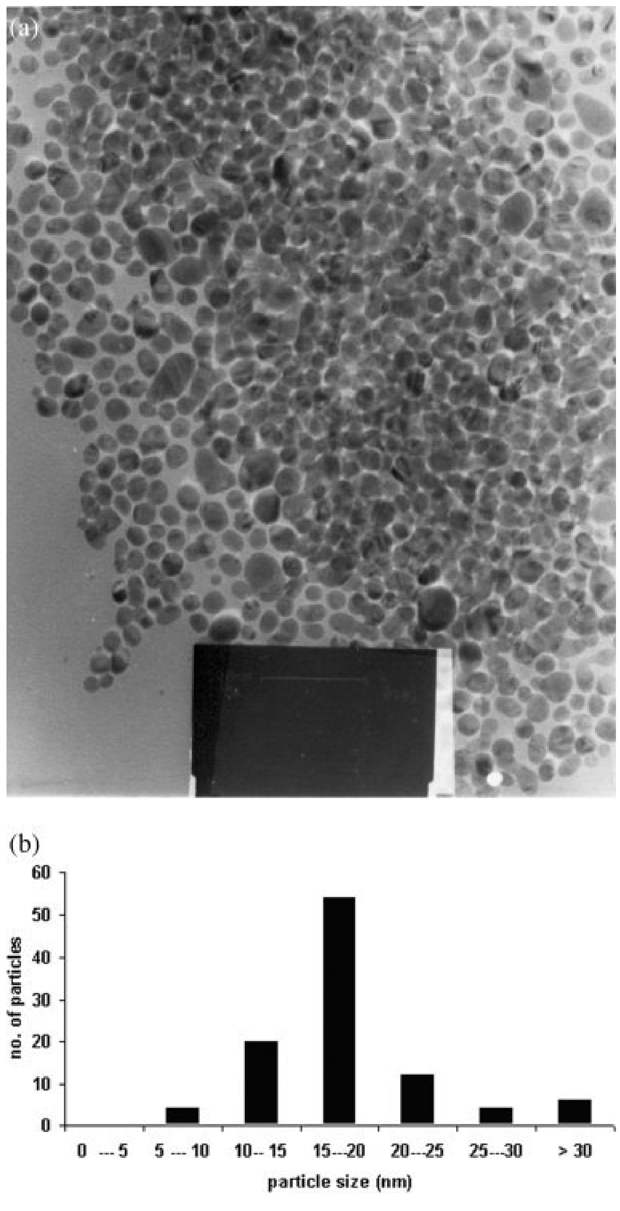

Figure 4. (a) TEM scans for silver nanoparticles in initial microemulsion at a magnification of 115,000; (b) PSD silver nanoparticles synthesized in initial microemulsion.

The scale bar represents 100 nm.

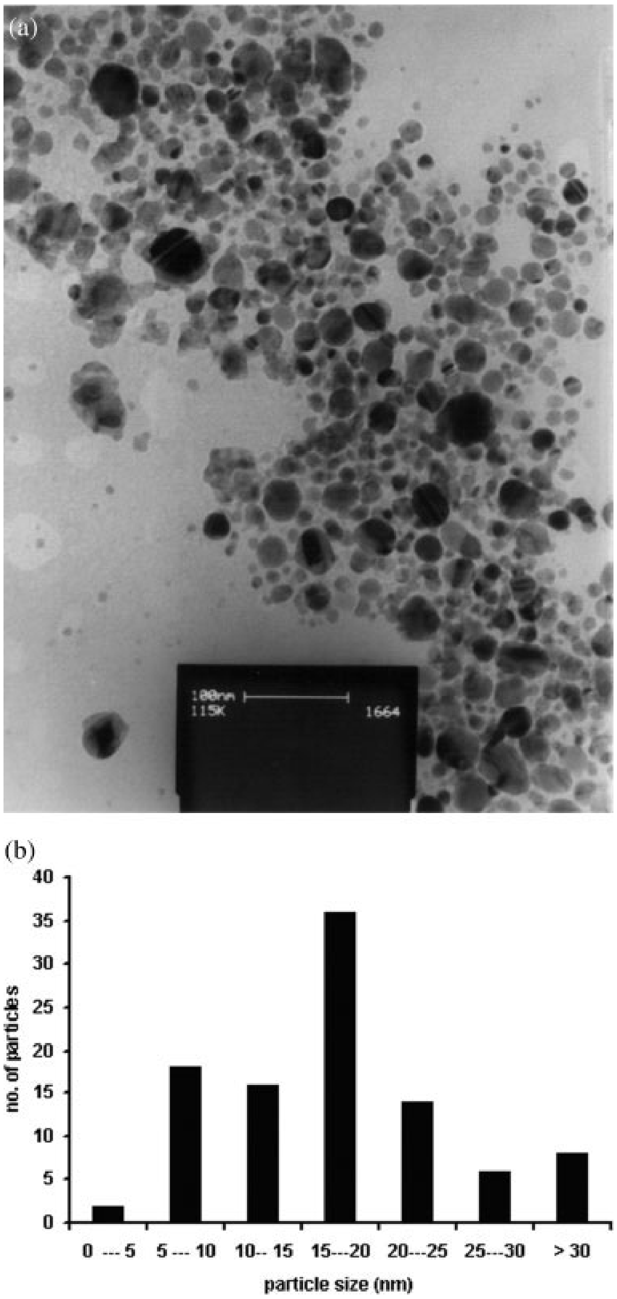

Figure 5. (a) TEM scans for silver nanoparticles in filtrate after first reuse at a magnification of 115,000; (b) PSD silver nanoparticles synthesized in filtrate after the first reuse.

The scale bar represents 100 nm.

(0.05 mol dm^{-3}) was added, in both the cases no reddish brown coloration due to formation of silver nanoparticles was observed, indicating absence of silver nitrate and sodium borohydride in the filtrate 1.

Preparation of nanoparticles in reuse 1 and reuse 2 batches

To prepare a second batch (reuse 1) of nanoparticles, the filtrate 1 was divided into two equal parts; required amount of solid silver nitrate was added to the first part to prepare a microemulsion containing 1.8 × 10^{-3} mol dm^{-3} silver nitrate solution. Required amount of solid sodium borohydride was added to the second part, to prepare a second microemulsion containing 9 × 10^{-4} mol dm^{-3} sodium borohydride solution. The R value was maintained at 10. The microemulsion containing sodium borohydride was added at once to microemulsion containing silver nitrate. The mixture was shaken for 2 h to produce a third microemulsion containing silver nanoparticles (reuse 1 batch). The reuse of two batches of nanoparticles was prepared by following exactly the same procedure for separation of nanoparticles, and the addition of reactants as in reuse 1. The reuse 1 and reuse 2 batches of

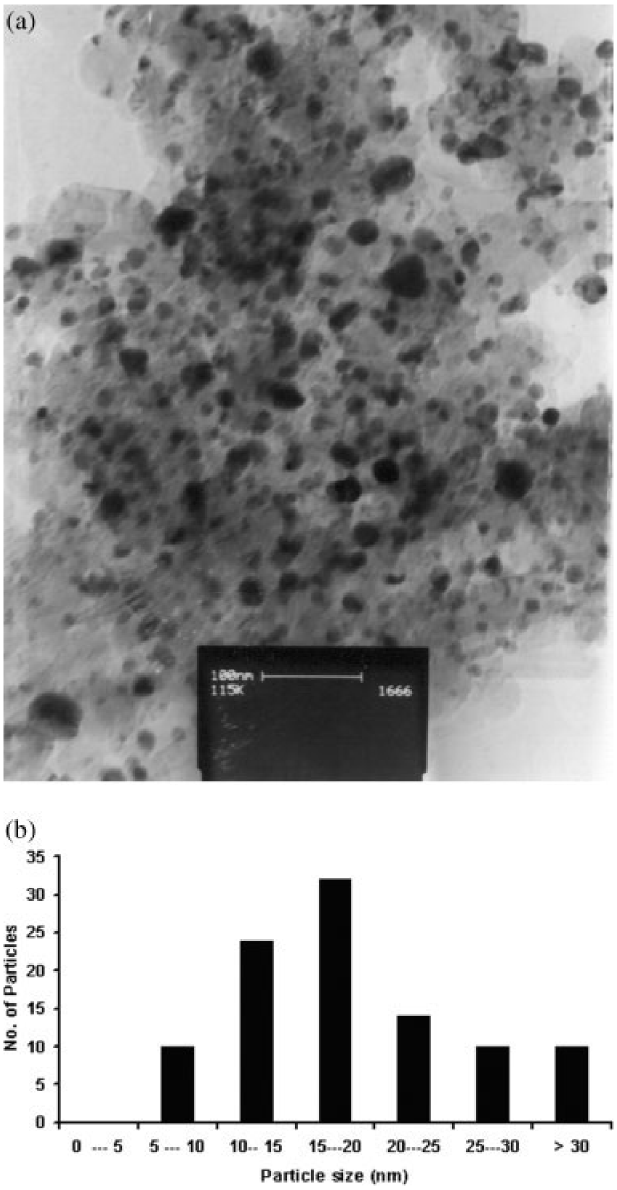

Figure 6. (a) TEM Scans for silver nanoparticles in filtrate after second reuse at a magnification of 115,000; (b) PSD silver nanoparticles synthesized in filtrate after second reuse.

The scale bar represents 100 nm.

nanoparticles were characterized by UV-visible spectroscopy and transmission electron microscopy exactly in the same manner as the first batch of nanoparticles.

Results and Discussion

UV-visible spectra

UV-vis spectra have been proved to be quite sensitive to formation of silver nanoparticles.[4] The water-in-oil microemulsions, containing nanoparticles were used directly for absorption studies. Same standard blank microemulsions (without reactants) were used as a reference in UV-vis spectrophotometer. Figure 3 shows the absorption spectra of the silver nanoparticles produced in the initial AOT/heptane/water system, after surfactant reuse (reuse 1 and reuse 2), and also the filtrate. Looking at relative heights of peaks in Figure 3, we can conclude that silver nanoparticles are present in the reused batches, and that amount of silver nanoparticles left in the filtrate is negligible. We, can, thus, conclude that the separation method is fairly efficient.

The absorption peak at 410 nm is characteristic absorption peak of silver nanoparticles.[4] Nanoparticles formed after reusing the surfactant shows absorption very similar to those formed in the first run (Figure 3).

TEM, PSD and Stability

Figure 4a shows the TEM photographs of silver nano particles produced in the first run at 1 lakh magnification. The particles are more or less spherical in shape. Figure 4b shows the particle-size distribution of these particles. The particle sizes were determined by using the software Image pro plus. The average size of the particles was 18.2 nm. From the particle-size distribution we observe that 94% particles were within 5–30 nm with 54% being in the range of 15–20 nm. About 6% particles were greater than 30 nm.

Figures 5a and b show the TEM photographs and particle-size distribution, respectively of silver nanoparticles synthesized after first reuse. These nanoparticles are also spherical in shape, and the average size of particles was 18.7 nm. From the particle-size distribution we observe that 36% particles are within 15–20 nm, and 8% of particles are greater than 30 nm.

Figures 6a and b show the TEM and particle-size distribution for silver nanoparticles synthesized after the second reuse. We get spherical particles with average size 18.25 nm, and about 32% particles in the 15–20 nm size range, and 10% of particles were greater than 30 nm.

The stability of the silver nanoparticles formed in both fresh AOT solution and reused surfactant was observed for three weeks. The silver nanoparticles showed no aggregation or separation, and remained stable in the microemulsion in both fresh, as well as reused surfactant (after reusing twice). Figures 7a and b show the UV-visible spectra of silver nanoparticles synthesized in original AOT, and reused surfactant (filtrate 2), respectively, at different time intervals. (From 48 h to three weeks). We can observe from Figures 7a and b that there is no significant change in the plasmon absorption peak of silver nanoparticles in the microemulsions, both in the case of fresh and reused surfactant.

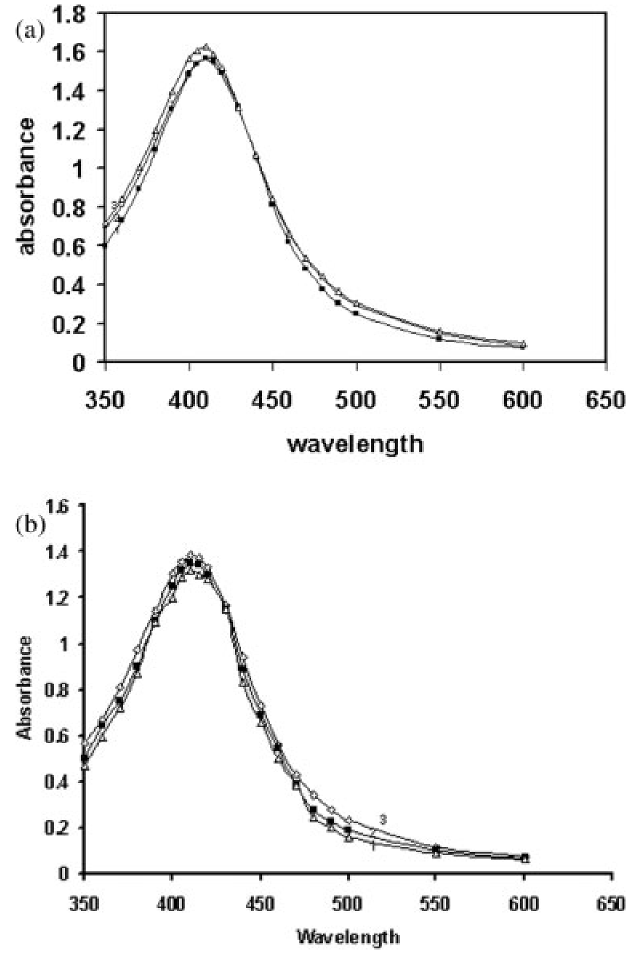

Figure 7. (a) Absorbance spectra of silver nanoparticles in original AOT microemulsion at different time intervals; (b) absorbance spectra of silver nanoparticles synthesized in the filtrate after the second reuse at different time intervals.

(a) (1) (■) After three weeks, (2) (-) after two weeks, and (3) (△) after 48 h. (b) (1) (△) After three weeks, (2) (■) after two weeks, and (3) (◇) after 48 h.

We can conclude from these data on particle-size distributions and UV-visible spectra that the geometric characteristics, and the chemical content of the nanoparticles formed by reused surfactant/organic phase remain virtually the same as fresh surfactant/organic phase. Moreover, the nanoparticles remain stable in the microemulsion made of reused surfactant/oil phase. Therefore, the reuse of surfactant and organic phase is a good possibility.

Acknowledgments

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